PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
Volume 15 June 15, 1929 Number 6

THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT MODERATELY LOW PRESSURES

By H. C. Ramsperger, M. E. Nordberg and R. C. Tolman
Gates Chemical Laboratory, California Institute of Technology

Communicated May 13, 1929

1. *Introduction.*—At moderately high pressures, the decomposition of gaseous nitrogen pentoxide was shown by the original work of Daniels and Johnston[1] to be homogeneous and of the first order and this has been completely confirmed by the work of subsequent investigators.[2] At low pressures, however, there has been a striking lack of agreement as to the rate of decomposition of this substance.

Hirst and Rideal,[3] Hibben,[4] and Loomis and Smith[5] have all tried to follow the rate of the decomposition at low pressures by freezing out the nitrogen oxides during the course of the reaction and measuring the pressure of the oxygen which had been formed. Working at initial pressures in the range 0.035–1.450 mm. of mercury Hirst and Rideal report that the specific rate of decomposition becomes greater at low pressures, the increase in rate being appreciable at 0.25 mm. and several fold at their lowest pressures. Hibben, on the other hand, working in the pressure range 0.03 to 0.18 mm. finds throughout the same specific rate of decomposition as at high pressures. Loomis and Smith, however, conclude that the method used in all three sets of experiments is unreliable, since, in the first place, they find that appreciable amounts of oxygen can be occluded and carried down with the condensed oxides of nitrogen, and in the second place, find that nitrogen pentoxide is appreciably adsorbed on the surface of pyrex glass.

More recently Sprenger[6] has attempted to follow the rate of decomposition by pressure measurements made with a quartz fibre gauge. Working in the range 0.01 to 0.05 mm. pressure, he comes to the extraordinary conclusion that the nitrogen pentoxide decomposes at approximately its high-pressure rate when it is first introduced into the reaction flask, and later, with a considerable fraction of the original nitrogen pentoxide still remaining, it ceases to decompose at all.

Finally, Rice, Urey and Washburne[7] report that preliminary measure-

ments made by Miss E. Wilson show that the specific rate of decomposition of nitrogen pentoxide falls below the high-pressure rate even at pressures of several millimeters.

Since the low-pressure rate of homogeneous gas reactions is of great theoretical interest, especially in connection with the theory of activation by collision as developed by Rice and Ramsperger[8] and by Kassel,[9] further work on the low-pressure rate of decomposition of nitrogen pentoxide seems desirable in view of the almost complete lack of agreement in the results described above.

2. *Special Features of the Present Experimental Method.*—In selecting an experimental method for the present work, special attention was paid to the elimination or minimization of the possible sources of error which appeared to us as most dangerous in work of this kind.

The possibility of occlusion of oxygen and the recurring disturbance in the condition of the decomposing gas, which occur when the reaction is followed by periodically freezing out the oxides of nitrogen and measuring the pressure of the residual oxygen, were eliminated by arranging to follow the course of the reaction by a direct measurement of the total pressure. This was accomplished by the use of a modified form of the "click" gauge originally devised by Smith.[10] The essential part of this gauge consists of a thin bulb of glass with a flattened side or diaphragm containing a wrinkle which produces a small clicking sound when the pressure difference on the two sides of the bulb is adjusted to a point where an inward or outward motion of the diaphragm occurs. The modifications introduced to make the gauge suitable for our low pressures consisted, (*a*) in making the diaphragm extremely thin so that the "click constant" or pressure difference necessary to operate the gauge was not too large compared with the pressures that were to be measured, (*b*) in attaching a microphone button on the tube leading to the gauge which made it possible to hear the click in a telephone receiver, and (*c*) in arranging a McLeod gauge to measure the small external pressure when the gauge clicked. The pressure readings thus obtained appeared to be reliable to about 0.01 mm. of mercury.

The dangers arising from the adsorption of gases on the walls of the reaction vessel were minimized in the following way. In the first place, we reduced the ratio of surface to volume by using an extraordinarily large reaction vessel, which was constructed from a 45-liter glass flask. In the second place, we cleaned the inside surface of the flask solely by wiping with a clean towel, and allowed *no* cleaning solution or other liquid to come in contact with it.[11] Finally, before each set of runs, the flask was heated to about 70°C. and pumped to a high vacuum before use, and furthermore before each set of runs nitrogen pentoxide was introduced into the flask and pumped out in order to condition the surface.

In addition to the dangers of adsorption on the surface, we also recog-

nized that the actual collision of molecules with the surface may be undesirable in producing an abnormal amount of molecular activation or deactivation as compared with that arising in the interior of the reacting mixture from the mutual collisions of the gas molecules themselves. This was an additional reason for going to the unusually large reaction vessel.

3. *The Apparatus and Experimental Procedure.*—The reaction was carried out as stated above in a 45-liter flask. This flask was placed in a specially constructed air thermostat, with suitably lagged walls and cover, and provided with air circulation and heating coils. The temperature was held constant throughout each run to within 0.05°C., but showed by soundings a maximum variation of 0.2 to 0.3°C. between different parts of the thermostat. This variation was allowed for by averaging and the final figures given are believed to be reliable to about 0.1°C.

The flask available was made of soft glass and was provided with a short "ring neck" about 4″ in diameter, the reinforced ring being approximately $1/2$″ thick and ground to a flat surface. The closing of the flask was effected by the use of a cap of plate glass, $3/8$″ thick, which was ground against the flat surface of the ring, while a 1″ glass tube leading to the "click gauge" and auxiliary apparatus was ground into a taper hole in this cap. The two ground glass joints were made tight by painting on the outside under vacuum with "Duco" lacquer. The bright red color of this material permitted us to determine the extent to which the lacquer had "crept" into the ground glass joints, and this did not appear sufficient to be serious.

The reaction flask was connected directly to the "click gauge" and through a stopcock to a smaller "fore flask" of a suitable size for containing the sample of pentoxide to be used. This "fore flask" was connected through stopcocks to a side trap containing the supply of solid pentoxide, to mercury diffusion pumps protected by a trap for freezing out mercury vapor and oxides of nitrogen, and to a McLeod gauge which could be used in the absence of nitrogen pentoxide for a direct measurement of the pressure in the reaction flask. The stopcocks were lubricated with a special high vacuum preparation.[12]

The nitrogen pentoxide was prepared from ozone and nitrogen dioxide, dried by passage through phosphorous pentoxide, and was condensed out in the side trap already mentioned, which was then sealed off from the preparation train and kept immersed in ice water. Samples of pentoxide were introduced into the reaction flask by first pumping the supply of condensed pentoxide free from its decomposition products, and then allowing evaporation to take place into the previously evacuated "fore flask," followed by admission into the evacuated reaction flask.

Before each run and in some cases after the run, the "click constant" or pressure difference necessary to operate the "click" was determined with

a high vacuum on the reaction side of the "click gauge" diaphragm. In case of a difference, the "click constant" determined before the run was used for correcting the pressures measured during the run, and the "click constant" determined after the run was used for correcting the final pressure. This difference was 0.03 mm. in the worst case.

At the end of the runs, a slight grayish deposit was found on the inside surface of the reaction flask. We believe this to have been produced from mercury vapor which in spite of our precautions must have entered the flask. It does not appear to have affected the constancy of our results.

TABLE I

Run No. 1. Temperature = 37.30°C. Click constant = 4.200 mm.

TIME SECONDS	PRESSURE ON McLEOD MM.	PRESSURE IN REACTION FLASK MM.	PRESSURE OF N_2O_5 MM.	SPECIFIC REACTION RATE $k(\text{SEC.}^{-1}) \times 10^4$
0				
110	6.244	2.044	0.826	
390	6.280	2.080		1.77
980	6.420	2.220	0.708	
1626	6.518	2.318		1.74
2310	6.636	2.436	0.562	
2980	6.732	2.532		1.65
3670	6.802	2.602	0.449	
3978	6.836	2.636		1.71
4770	6.916	2.716	0.372	
5696	7.004	2.804		1.62
6580	7.056	2.856	0.277	
6790	7.080	2.880		1.70
7850	7.154	2.954		
8988	7.192	2.992	0.184	
10980	7.268	3.068		
15570	7.354	3.154		
20670	7.412	3.212		
∞	7.460	3.260	0.000	
			Av.	1.70
			Mean deviation	0.04

4. *Experimental Results.*—Using the apparatus described above, 12 runs were made on the rate of decomposition of nitrogen pentoxide. Of these, Run 2 was not carried to completion since the data obtained showed a large total pressure of gas with only a small proportion of pentoxide. Run 5 was discarded because the reaction vessel had contained air before the run and the surface had not been conditioned by pumping out at a *high* temperature and by admitting and pumping out a preliminary charge of pentoxide, as was done in all other cases after the vessel had contained air. It gave a high "constant" which fell off during the run. Finally, Run 6 was discarded because of failure to obtain a sufficient quantity of pentoxide to measure with any accuracy.

To give an idea of the course of the 9 successful runs, we present below, in tabular form, the complete data for our highest pressure Run 1 in which the agreement of the different constants among themselves is good, and our lowest pressure Run 10, in which the agreement is necessarily much less good. Run 1 was carried out with material which had been only once condensed and presumably consisted originally of a mixture of pentoxide and dioxide, as shown by comparing the first measurement of total pressure with the pressure of pentoxide present. Run 10 on the other hand was carried out with material resublimed in a stream of ozone which gave us pure pentoxide, as indicated by the approximate check between the first measurement of total pressure and the pressure of pentoxide present.

TABLE II

Run No. 10. Temperature = 30.94°C. Click constant = 0.870 mm. (new diaphragm)

TIME SECONDS	PRESSURE ON McLEOD MM.	PRESSURE IN REACTION FLASK MM.	PRESSURE OF N_2O_5 MM.	SPECIFIC REACTION RATE $k(\text{SEC.}^{-1}) \times 10^4$
0				
215	1.060	0.190	0.1924	
1183	1.088	0.218	0.1737	1.06
1850	1.106	0.236	0.1617	1.07
2830	1.120	0.250		0.68
4070	1.140	0.270	0.1390	
5320	1.164	0.294		0.82
6740	1.181	0.311	0.1116	
8675	1.203	0.333		0.73
10950	1.225	0.355	0.0822	
14400	1.254	0.384	0.0628	0.78
17690	1.275	0.405		0.59
21425	1.286	0.416	0.0414	
58080	1.326	0.455		
∞	1.348	0.478	0.0000	
			Av.	0.818
			Mean deviation	0.141

The successive columns of the tables give the time in seconds measured from the instant when the reaction flask was closed off, the pressure necessary to operate the "click" as measured by the McLeod gauge, the total pressure in the reaction flask, the calculated pressure of pentoxide, and values of the specific reaction rate corresponding to the intervals indicated. The pressure in the reaction flask was obtained from the reading of the McLeod gauge by subtracting the "click constant." The pressure of pentoxide present at any time was calculated from the final pressure, making a correction for the degree of association of nitrogen dioxide to tetroxide, which was very small at these low pressures. The specific reaction rates were calculated on the basis of first order decomposition for intervals so chosen as to give a fair picture of the course of the reac-

tion. This was done by dividing the run into a reasonable number of intervals (5–9) in which approximately equal increases in pressure occurred. The first pressure reading was not used in three cases, since it did not fall on the smooth curve. This may have been due to haste in trying to adjust for the click. The interval method of calculation was chosen since it gives a fairer idea of any trend in the reaction even though it gives a poorer check among the constants. In no case was there any evidence of a trend in the reaction rate, except for the apparent trend in Run 10, which presumably is due to the inaccuracies of measurement in this very low-pressure run.

A summary of the final results for all 9 runs is given in the last table which is self-explanatory. In Runs 1–4, we used material which had been only once condensed and consisted of a mixture of pentoxide and dioxide as indicated by the first pressure measurement. In all the other runs, however, we used resublimed material and obtained in every case an approximate check between the first pressure measurement and the calculated pentoxide present at the start.

SUMMARY OF RESULTS

RUN NO.	TEMP. °C.	INITIAL PRESSURE IN FLASK MM.	NO. CONSTANTS CALCULATED	AVERAGE RATE CONST. (SEC.$^{-1}$) $\times 10^4$	MEAN DEVIATION	HIGH PRESSURE RATE CONSTANT (SEC.$^{-1}$) $\times 10^4$
10	30.94	0.190	7	0.818	0.141	0.775
12	30.76	0.789	7	0.736	0.056	0.757
11	30.76	0.890	9	0.739	0.049	0.757
4	36.84	0.380	8	1.57	0.32	1.70
3	36.80	0.884	8	1.56	0.13	1.68
1	37.30	2.044	6	1.70	0.04	1.79
9	41.97	0.397	5	3.11	0.41	3.25
7	41.98	0.700	8	3.31	0.18	3.25
8	42.00	0.710	8	3.17	0.23	3.25

5. *Conclusion.*—For comparison we have given in the last column of the final table the *high pressure* rate of decomposition of nitrogen pentoxide, as obtained from the data of Daniels and Johnston, by taking the best straight line through a plot of their values of log k against $1/T$ for the temperatures 25°, 35°, 45°, 55° and 65°. The agreement between our constants and theirs is probably within the experimental error of either piece of work.

We may conclude that, down to the pressure range that we have investigated, nitrogen pentoxide shows no change in its specific first-order rate of decomposition. It should be particularly noted that there is no falling off in the rate, in contradiction to the preliminary result of Miss Wilson of a falling-off at pressures of several millimeters, as reported by Rice, Urey and Washburn.

The behavior at still lower pressures is a matter of great interest. We

hope to obtain data on this in the near future by using a different method of pressure measurement.

[1] Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

[2] For a bibliography of experimental work on nitrogen pentoxide, and tests of the constancy of high pressure rate, see Rice and Getz, *J. Phys. Chem.*, **31**, 1572 (1927).

[3] Hirst and Rideal, *Proc. Roy. Soc.*, **109A**, 526 (1925).

[4] Hibben, *J. Am. Chem. Soc.*, **50**, 940 (1928).

[5] Loomis and Smith, *J. Am. Chem. Soc.*, **50**, 1864 (1928).

[6] Sprenger, *Zeit. physik. Chem.*, **136**, 49 (1928).

[7] F. O. Rice, Urey and Washburn, *J. Am. Chem. Soc.*, **50**, 2402 (1928).

[8] O. K. Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); *Ibid.*, **50**, 617 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928).

[9] Kassel, *J. Phys. Chem.*, **32**, 225 (1928); *Ibid.*, **32**, 1065 (1928).

[10] D. F. Smith and Taylor, *J. Am. Chem. Soc.*, **46**, 1393 (1924).

[11] The flask was taken from stock but as far as we are aware had not previously had liquid in it.

[12] Obtainable from Metropolitan Vickers Electric Co., Ltd., Strafford Park, Manchester, England.

TYPES OF UNIMOLECULAR REACTIONS

BY OSCAR KNEFLER RICE[1]

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated May 15, 1929

Recently certain writers have expressed the belief that chemical reactions are to be explained on the basis of the quantum mechanical resonance phenomenon.[2] There are a large variety of different types of chemical reactions, of different degrees of complication, some of which may be too complicated to treat directly by quantum mechanical methods, but some of which are so simple that they have already been treated in more or less detail on the basis of the new mechanics. In this situation it seems desirable to point out the relations between certain reactions, one of which has been considered on the basis of the quantum mechanics, and the others of which have been treated only by classical or old quantum theory methods. We hope later to consider some of these relations in more detail with a view to seeing whether we can make new inferences (even though they must necessarily be of a preliminary nature) about the more complicated reactions.

The types of reaction which we wish to consider are predissociation, unimolecular decompositions of complex organic compounds, and photochemical decomposition of the same compounds, all occurring in the gaseous state.

1. *Predissociation.*—Predissociation can occur when a molecule can

be excited by absorption of radiation of a given frequency in two different ways, i.e., by two different electronic jumps, accompanied by the corresponding changes in vibrational and rotational quantum numbers. If one of these electronic states has a lower dissociation limit than the other, the continuum corresponding to the former overlaps discrete vibration rotation levels of the other. Thus a molecule in one of these discrete states (a predissociated molecule[3]) may be able to go by a radiationless transition to the overlapping continuum, and dissociate. This is a purely mechanical process occurring after the molecule has been activated by light. The theory of this sort of transition has been treated by a number of writers.[4]

2. *Unimolecular Decompositions.*—At first sight it may seem a far cry between the decomposition of a complicated molecule and predissociation; but, though outwardly the differences appear great, there are certain striking similarities. In the first place the theory of the decompositions indicates that only those molecules may react which have energy greater than a certain minimal amount, i.e., the molecules must be activated. In these cases, however, the molecules presumably do not obtain the energy by absorption of light, but by collision with other molecules, and the energy is presumably not electronic energy, but simply the energy of vibration of the atoms within the molecule. These reactions have been extensively treated using classical and old quantum theory statistical methods.[5] By these considerations it seems to have been rather conclusively proved (at least in the cases of azomethane[5] and methyl isopropyl diimide[6]) that the actual decomposition of a molecule occurs only when the requisite energy becomes localized in a certain part of the molecule (say a certain oscillator). Thus there are certain states of the molecule in which it has sufficient energy but does not decompose until a radiationless transition from a discrete state to a continuous state takes place. This is seen to be in very close analogy with the case of predissociation, only in the present case the transition consists of a change from one vibrational state to another, rather than from one electronic state to another.

3. *Photochemical Decompositions.*—In the case of the photochemical decomposition of a complex molecule we have a still more complicated situation, there being presumably first an electronic excitation, very likely followed by transitions of the type mentioned in the preceding paragraph, in which exchanges of energy occur between oscillators. This is similar to the suggestion of Ramsperger[7] made in connection with the photochemical decomposition of azomethane, but there is no necessity of a direct transfer of energy from the excited electron to the oscillators in the molecule, as the very fact that the electron is excited may very likely alter the binding forces in the molecule in such a way that oscillation is started which ultimately leads to decomposition. Thus after

excitation some of the oscillators will find themselves far from their new positions of equilibrium and will begin to vibrate so that some of the light absorbed actually goes to exciting atomic vibrations, as described by Franck in simpler cases, and, furthermore, it is not at all unlikely that the dissociation energy in the new state will be lowered. In the case of the photochemical decompositions, as in the other cases, the final reaction probably occurs as a transition from the predissociated condition just described to a continuous state with the same energy.

It should be noted that the reactions described above are not of the radioactive type, in which there is a leaking away over a potential energy hump. The energy curve of the oscillator which breaks *may* have such a hump in it, to be sure, but the *essential* process, in the belief of the present writer, contrary to the view recently expressed by Bourgin,[8] is a quantum transition which cannot be properly described as a leaking over a hump, but must be described as we have done above.

In closing it may be well to mention briefly the probable nature of one inference regarding reactions of type 2 which we will be able to make from the quantum mechanical theory of reactions of type 1. When there is interaction between continuous states and discrete states (i.e., when it is possible for radiationless transitions to take place between discrete and continuous states in the manner we have described) it has the effect of broadening the discrete states. (The exact meaning of this statement is given in my article previously referred to.[4]) When there is interaction between a set of continuous states and several discrete states, these discrete states may be broadened till they overlap, even though the unperturbed discrete states were of different energies. This means that the perturbed eigenfunctions which correctly describe the conditions of the molecule will be functions of a number of unperturbed eigenfunctions corresponding to different energy values. (The unperturbed eigenfunctions are those which would correctly describe the molecule if the radiationless transitions could not occur.) The broadening of the discrete lines is probably in general inversely proportional to the life period of the molecule in the discrete state, so at least where the reaction rate is fast the result will be a considerable complication of the statistics of the molecule, which we hope to treat later in more detail.

The ideas expressed in this note seem to be in direct contradiction to the view expressed by Langer[9] that reaction occurs when a molecule passes from one discrete state to another; it hardly seems possible that his views can be correct in the case of a decomposition, where the final state to be reached is one of a continuous series.

[1] NATIONAL RESEARCH FELLOW.

[2] Oppenheimer, *Phys. Rev.*, **31**, 81 (1928); Langer, *Phys. Rev.*, **33**, 290 (1929); Kallmann and London, *Zeits. physik. Chem.*, **2B**, 207 (1929).

[3] We have defined predissociation in possibly a slightly more specialized sense than that first used by Henri and Teves, *Nature*, **114**, 894 (1924).

[4] See e.g., Kronig, *Zeits. Physik*, **50**, 360 (1928); Rice, *Phys. Rev.*, **33**, 748 (1929).

[5] Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927), **50**, 617 (1928); Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928); Rice, *Comptes Rendus, Réunion Internationale de Chimie Physique*, Paris, October, 1928.

[6] Ramsperger, *J. Am. Chem. Soc.*, in press.

[7] Ramsperger, *Ibid.*, **50**, 123 (1928).

[8] Bourgin, *Proc. Nat. Acad. Sci.*, **15**, 357 (1929).

[9] Abstract No. 127 presented to the American Physical Society at the Washington meeting, April 18–20, 1929.

THE VALENCE OF SULFUR IN DITHIONATES

BY RALPH E. WINGER AND DON M. YOST

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated April 19, 1929

It has been shown by Lindh[1] and others[2] that the shift in the K absorption edges for various compounds of sulfur, chlorine, phosphorous, iron, and some other substances, depends chiefly on the valence of the element in a given compound. With increasing valence in a given element the wave-length of the edge shifts to smaller values. Stelling[3] has explained the effect of valence as being due to the screening effect of electrons in external parts of atoms. To be sure, other factors influence the position of the edges, such as other elements occurring in the compounds, and lattice structure, but these factors produce in general only minor fluctuations around a mean value, whereas the mean values for the several valences show rather wide divergences. For example, the wave-lengths of the principal K edge of a large number of 4- and 6-valent inorganic sulfur compounds practically all lie within half an X-unit of the means of their respective groups, whereas the means themselves are separated by 8 X. U. A similar state of affairs is observed in the 2-valent compounds. The edges do not lie quite so close to the mean, but the mean is 13 X. U. from that of the 4-valent compounds. All the substances thus far investigated bear out the general statements above.

In view of the rather large body of facts now before us, it seems legitimate to try to use x-ray absorption data to obtain information on the valence state of an element in a compound.

The substance used in the present investigation was potassium dithionate, the object being to determine the state of the two sulfur atoms in $K_2S_2O_6$. Lindh[4] has already shown that for $Na_2S_2O_3$ and some other thiosulfates there is not just a simple absorption edge, but two edges, corre-

sponding in position to the valence states SII and probably SIV, which states are generally assumed by chemists for the two sulfur atoms in the thiosulfates. Now if valence is calculated in the usual way, then on the assumption that the sulfur atoms of the dithionates are in the same state we get for them a valence of V, and we would expect to find the K absorption edge corresponding to a single state, rather than the two edges shown by the thiosulfates.

In the present work we found as a matter of fact only one edge for $K_2S_2O_6$, and its position lies between Lindh's measurements for 4- and 6-valent sulfur. Lindh's mean values are:

SVI	K_1	4987.9 X. U.
SIV	K_1	4996.0 X. U.

Our present measurements show for $K_2S_2O_6$

S	K_1	4992.8 X. U.

This result, intermediate between the usual values of SIV and SVI, seems to indicate that the sulfur atoms are equivalent. Our view is supported by the space group determination[5] of the same compound, and also by the general chemical behavior of the dithionates.

The exposures were made in an x-ray vacuum spectrograph of the Siegbahn type, using a slowly rotating crystal of calcite as analyzer. The absorbing screen consisted of finely powdered potassium dithionate on tissue paper, inserted between the slit and the crystal. The slit width was slightly under 0.1 mm., and the distances of crystal from slit and plate, respectively, were each about 18 cm. The wave-length we give is based on Lindh's value for K_2SO_4. We made comparison plates, using this material, and determined the shift by noting the distance of the edges from a mechanical reference line photographed at the same place on each plate.

The absorption edges so obtained leave something to be desired in sharpness, as they appear rather fuzzy under the comparator. The difficulty of determining the proper location of the edge has been discussed by Stelling.[6] The ordinary comparator method was used, and later another method, which will be briefly described. The two plates to be compared for shift are mounted at right angles to each other, one of them being fixed to a carriage which can be moved by a micrometer screw. Beams of light, after passing normally through the two plates, are made parallel by means of a half-silvered surface between two prisms, and the two beams before entering the prisms are cut off by straight edges in such a way that any lines or edges to be compared are viewed directly end to end. The reference lines can be brought easily and accurately into juxtaposition, and the shift in edge can then be measured directly by turning the micrometer until the edges coincide. If the edges are of about the same degree of fuzziness (and in the present case they appeared to be so),

it is no longer necessary to speculate on their proper location. The method suffers from the difficulty usual in comparators—lack of contrast—but is rapid and direct and permitted us to duplicate readings to within 2 or 3 hundredths mm., corresponding to a wave-length difference of about two or three tenths of an X. U.

[1] Siegbahn, *Spectroscopy of X-rays*, Chap. V., 1925.

[2] Otto Stelling, *Zs. Phys.*, **50**, 506, 1928; Aoyama, Kimura, and Nishina, *Zs. Phys.*, **44**, 810, 1927; G. A. Lindsay and H. R. Voorhees, *Phil. Mag.*, **6**, Suppl., 910, 1928.

[3] Otto Stelling, loc. cit.

[4] Siegbahn, loc. cit.

[5] M. Huggins, *Phys. Rev.*, **31**, 916, 1928.

[6] Otto Stelling, loc. cit.

STUDIES ON THE GROWTH OF ROOT HAIRS IN SOLUTIONS. THE pH MOLAR-RATE RELATION FOR BRASSICA OLERACEA IN CALCIUM SULPHATE

BY WANDA K. FARR*

Communicated April 13, 1929

Earlier studies* upon the elongation of root hairs in solutions of single calcium compounds by C. H. Farr and W. K. Farr have shown a very delicate reaction of these particular cells to concentrations of the salt as well as to the various hydrogen-ion concentrations of the solutions used. By means of an apparatus constructed especially for the investigations, seedlings of uniform length and equal age were kept in flowing solutions of definite hydrogen and hydroxyl-ion concentrations, for periods of about twenty hours. Temperature conditions were maintained between 19°C. and 21°C. throughout the series of experiments. The work was carried on in basement dark rooms of the Marine Biological Laboratory at Woods Hole, Mass., during the summers of 1925, 1926 and 1927. By means of special micrometer eye-pieces readings were taken at ten-minute intervals for three hours daily upon the rate of elongation of aquatic root hairs. Careful observations upon other features of root development were also made and were compared with the root-hair development.

The complete absence of growth of root hairs in pure distilled water, along with the definite rates of growth in different concentrations of $Ca(OH)_2$, established at the outset a basis for the comparison of the behavior of root hairs in the presence and in the absence of the cation, Ca. Subsequent experiments in solutions of $CaCl_2$ and $Ca(NO_3)_2$ furnished data concerning the rates of growth in the presence of an additional anion.

* Aided by a grant from Bache Fund of National Academy.

The culture solutions in the first of these latter experiments contained the cations Ca and H and the anions OH and Cl; in the second instance the cations Ca and H and the anions OH and NO_3. The acidity and alkalinity of the $CaCl_2$ solutions were adjusted by the addition of varying quantities of HCl and $Ca(OH)_2$; the comparable adjustment was made in the $Ca(NO_3)_2$ solutions by the addition of HNO_3 and $Ca(OH)_2$. This procedure made possible a series of pH values in each salt concentration without the introduction of a new ion.

The purpose of this method of investigation has been to find a new approach to the analysis of the effect of the various nutrient ions in the plant culture solutions. Through a graphic representation in three dimensions, the growth rates at various hydrogen and hydroxyl concentrations studied were shown. A comparison of these models indicates at once the difference in growth rates obtained in calcium hydroxide, calcium chloride and calcium nitrate, as effected by both the hydrogen-ion concentration and the salt concentration of the solution.

The present report deals briefly with the results of experiments conducted during the summer of 1928 upon the growth of root hairs of *Brassica oleracea* in solutions of calcium sulphate. The studies were made in a constant temperature room of the laboratories of the Henry Shaw School of Botany, Washington University, St. Louis, Missouri, and were financed by a stipend from the Bache Research Fund. Several improvements over the technique used in former experiments were made. Two Spencer microscopes, No. 40 H, with the movable stage mechanism located below stage, greatly facilitated the movements of the glass culture chambers in which the roots were grown. The pH determinations, made formerly by means of a complete series of the Clark colorimetric standards, were checked by the use of both the Youden quin-hydrone potentiometer and the Kletts-Beaver colorimeter. All of the distilled water for both stock and culture solutions was redistilled in a small pyrex still. The entire series of apparatus, including that for pH determination, culture solutions, and seed germination, was kept and used in the experimental dark room in order to eliminate temperature variations and to increase the rapidity with which H-ion determinations could be made.

The growth of both the amphibious and aquatic root hairs on the seedlings was studied in flowing solutions of calcium sulphate in which the hydrogen-ion concentration was maintained constant to within 0.1 of a pH during each daily experiment. The range of salt concentrations of the solutions extended from 0.000448 *M* to 0.0140 *M*. Rates of growth of forty root hairs were measured daily, after a thirteen-hour period of immersion in the solution to admit of the necessary adjustment of the roots to the aqueous environment.

The three dimensional graphs, A and B, represent the results of the

experiment from the standpoint of rate of elongation of root hairs. Two different views of the same graph are presented, the one (A) extending toward increasing, and the other (B) toward decreasing concentrations of $CaSO_4$, in order to show the modal differentiation in the different concentrations. A line drawn through the central points of the shorter dimension of the rectangular floor plan would represent a location of pH values of about 6.8, or neutrality. To the left of this line is the region of acidity increasing to pH 2.5; to the right is the region of alkalinity

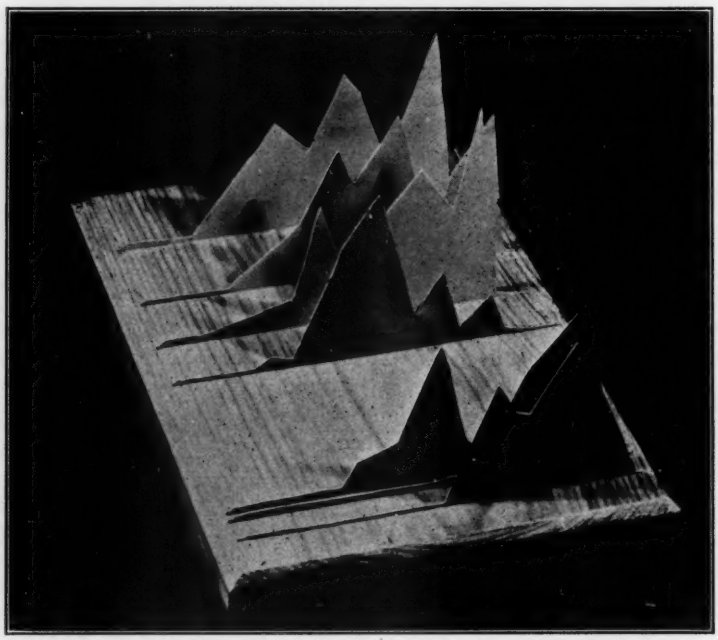


FIGURE A

Three-dimensional graph of the rate of elongation of root hairs of *Brassica oleracea* in solutions of calcium sulfate at various hydrogen-ion concentrations.

increasing to pH 12.0. These variations in acidity and alkalinity were carried out in all of the six salt concentrations of $CaSO_4$, represented by the exact line of location upon the floor plan of the upright models (2–7). The models themselves represent the rates of root-hair elongation at various hydrogen-ion concentrations of the following molar concentrations of $CaSO_4$: 0.000540, 0.000714, 0.00714, 0.0091, 0.0112 and 0.0140. Model (1) represents the rates of growth in $Ca(OH)_2$ solutions and serves, as formerly in the studies of $Ca(NO_3)_2$ and $CaCl_2$ solutions, as

a base line for the study of root-hair behavior in $CaSO_4$ solutions. It may be considered to be a 0.000000 M concentration with respect to the SO_4 ion.

The values for rates of growth in $Ca(OH)_2$ were obtained by the addition of varying quantities of saturated $Ca(OH)_2$ to distilled water. The amounts ranged from 0.5 cc. to 4.75 cc. and the resulting pH values of the solutions from 7–12.

Many very dilute solutions of $CaSO_4$ were studied at different hydrogen- and hydroxyl-ion concentrations by the addition of H_2SO_4 or $Ca(OH)_2$

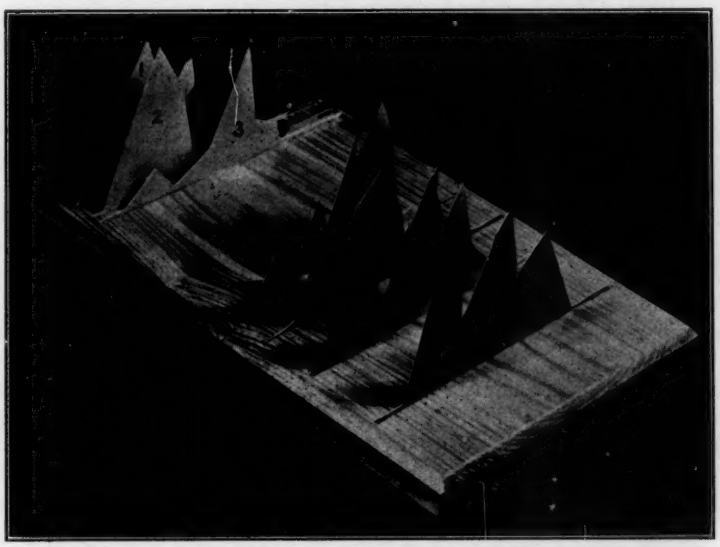


FIGURE B

A reverse view of the graph shown in A. Model (1) represents the rates of growth in $Ca(OH)_2$; models 2–7 the values obtained in solutions of $CaSO_4$.

to the known molar salt concentration. Below a salt concentration of 0.000448 M, however, the rates of growth obtained were so nearly equal to those obtained by the addition of $Ca(OH)_2$ to distilled water that the values were considered to be functions of the $Ca(OH)_2$ added to the solution. At a concentration of 0.000540 M $CaSO_4$ (Model 2) there would seem to be some evidence of the effect of the presence of the SO_4 ion. A comparison of the upright models (1) and (2) will show that a marked suppression of growth occurred in the neutral regions with a slight increase in growth in the alkaline region. The increase in rate of growth in the more alkaline solutions as compared with that in $Ca(OH)_2$ might

be considered to be due to the added nutritive value of the medium. The total absence of growth in the acid range may be tentatively interpreted as the results of the lack of Ca in sufficient concentrations to antagonize the effect of the H-ion. The suppression in the neutral range would seem to be difficult to explain upon any basis, especially when one considers the shifting of the highest mode in the next salt concentration, 0.000714 *M*, model (3), far toward the acid side, the alkaline optimum having been simultaneously suppressed. Upon any basis of consideration, one would seem to be justified in considering this region of salt concentration to be upon the borderline of anionic behavior with relation to the enlargement of root hairs. A more intensive study of such a region, at more frequent concentrations, would undoubtedly furnish interesting and perhaps more illuminating results.

Model (3) would then represent the first typical calcium sulphate curve obtained. The lowest concentration which will support growth over the same pH range lies at a point somewhere between 0.000540 *M* and 0.000714 *M*. The curve is typically bimodal with a slight suggestion of the trimodal curves which develop in higher concentrations. The low rates of growth in the alkaline range with the marked depression in rate of root-hair elongation at about pH 9 appears again in the following concentration studied, 0.00714 *M*, model (4). The suppression of growth at pH 9 also appears in all solutions of higher salt concentration.

Solutions of 0.00714 *M* show a new alkaline optimum between pH 8 and pH 9. This produces the trimodal type of curve for root-hair elongation which is typical of those in solutions of higher concentrations, changing only once, in 0.0112 *M*, where the curve for average rate of root hair elongation presents four modes and three means. The slight increase in growth rate at pH 4.4 in 0.00714 *M* solutions, creating a new acid maximum, is not continued in higher concentrations. It may be without significance.

In solutions of 0.0091 *M* concentration (model 5), the highest rate of root-hair elongation shifts far toward the alkaline side. The maximum rate of 130 microns per hour at pH 10 represents the highest numerical value for rate of root-hair elongation of *Brassica oleracea* in any solution of any salt of calcium studied by the present method.

While the two alkaline optima remain distinct in 0.0112 M solutions (model 6), the highest rate of growth has shifted toward the neutral part of the pH range. In the instance of such a slight change of modal location, however, one must always consider the possibility of error from experimental causes. The rates of growth found in this concentration as well as the next higher one are not strikingly different. In the latter, there is a return to a maximum growth rate in the alkaline region.

The highest concentration of $CaSO_4$ studied was determined, not by

the response of the root hairs, as in the instances of calcium chloride and calcium nitrate solutions, but by the limit of solubility of the salt in water at the given temperatures. The growth rate in 0.0140 M solutions (model 7) is well upheld over a wide range of hydrogen-ion concentrations. The plant would undoubtedly produce growing aquatic root hairs in calcium sulphate solutions of much higher concentration if it were possible to prepare them.

In general, the rates of growth obtained in solutions of $CaSO_4$ are slightly higher than those reported earlier in solutions of $Ca(NO_3)_2$, $Ca(OH)_2$, and $CaCl_2$. The differences are not great, however. It is only when we take into consideration the extremely dilute solutions employed in $Ca(OH)_2$ and $CaSO_4$ as compared with those used in $Ca(NO_3)_2$ and $CaCl_2$ that the point of real significance appears. If we are justified in interpreting the effect as due to the influence of the different anions, we find in a series representing degree of growth stimulation that $OH > SO_4 > Cl_2 > NO_3$.

This brief discussion may serve to point out the desirability of the present method of study in determining the effect of special ionic concentrations upon the process of cell enlargement. Correlated data from the same experiments, to be treated in the more extensive report of the study, would indicate that the root-hair reactions are in many instances similar to the reactions of the root as a whole to the environmental conditions. It may be found later that they are also indicative of the reactions occurring in the more complex phases of growth in response to these specific nutrient substances. From the combination of such simple figures as are shown here we might hope to construct a complex graphic representation of the growth reactions so common in plant-culture studies.

Summary.—1. A study of the rate of elongation of root hairs of *Brassica oleracea* has been made in solutions of calcium sulphate in concentrations extending from 0.000448 *M* to 0.0140 *M*.

2. Each salt concentration was studied over the entire range of hydrogen-ion concentrations at intervals of 0.5 pH units. The rates of growth obtained were, therefore, representative of a definite salt concentration at a relatively definite concentration of hydrogen and hydroxyl ions.

3. Solutions of $CaSO_4$ as dilute as 0.000448 will not support the growth of these root hairs.

4. A salt concentration of 0.000540 *M* produced excellent growth in the alkaline range between pH 8.5 and pH 10.5. The extent to which this growth is influenced by the $Ca(OH)_2$ added to increase the alkalinity of the solutions, as well as the absence of growth in the neutral and acid ranges at this concentration, is a matter for more detailed experimental consideration.

5. In the calcium sulphate experiments the first typical trimodal curve was produced when the concentration was increased to 0.000714 *M*. In

this, and in all higher concentrations, there were two distinct alkaline maxima and one acid maximum, showing close correspondence, in the different models, in their relative positions upon the pH scale.

6. The pH-Molar-Rate relation of root-hair elongation becomes clearer when interpreted in terms of a three-dimensional graph.

7. Compared with the rates of elongation of root hairs in solutions of calcium nitrate and calcium chloride, these results in calcium sulphate are notable for the high rate of growth in solutions of low salt concentrations.

8. The delicacy and the consistency with which these root hairs have responded to the definite concentrations of these simple nutrient solutions, and the ease with which accurate measurements of their elongation may be made, contribute greatly to their value as experimental material for study of this important phase of the growth process, cell enlargement.

STUDIES ON THE GROWTH OF ROOT HAIRS IN SOLUTIONS

FARR, C. F.:

1. "The Problem, Previous Work and Procedure," *Am. J. Bot.*, **14**, 446–456, 1927.
2. "The Effects of Concentrations of Calcium Nitrate," *Am. J. Bot.*, **14**, 497–515, 1927.
3. "The Effects of Concentrations of $CaCl_2$ and $Ca(OH)_2$," *Am. J. Bot.*, **14**, 533–564, 1927.
4. "The pH-Molar-Rate Relation for Collards in Calcium Chloride," *Am. J. Bot.*, **15**, 6–31, 1928.
5. "The Root Hair as an Index of Root Development," *Am. J. Bot.*, **15**, 103–113, 1928.
6. "Structural Responses of Collards to Calcium Chloride," *Am. J. Bot.*, **15**, 171–178, 1928.
7. "Further Investigations on Collards in Calcium Hydroxide," *Bull. Torr. Bot. Club*, **55**, No. 5, 223–246, 1928.
8. "Structural and Intracellular Features of Collards in Calcium Nitrate," *Bull. Torr. Bot. Club*, **55**, No. 9, 529–553, 1928.
9. "Root Hairs and Growth," *Quarterly Rev. Biol.*, **3**, No. 3, 343–376, 1928.
10. "The pH-Molar-Rate Relation for Collards in Calcium Nitrate," *Ann. Mo. Bot. Garden*. (In press.)

FARR, W. K.

11. "The Elongation of Root Hairs in Solutions of Single Calcium Compounds. A Comparison of Three Species: *Brassica oleracea; Avena sativa; Oryza sativa*," *Am. J. Bot.*, **14**, 627, 1927.
12. "Morphological Studies of Root Hairs of Oats and Rice in Solutions of Calcium Nitrate." (In preparation for publication.)

SOME NEW FEATURES OF THE ATMOSPHERIC OXYGEN BANDS, AND THE RELATIVE ABUNDANCE OF THE ISOTOPES O^{16}, O^{18}

BY HAROLD D. BABCOCK

MOUNT WILSON OBSERVATORY, CARNEGIE INSTITUTION OF WASHINGTON

Read before the Academy April 22, 1929

Accurate values of certain constants associated with the atmospheric oxygen bands and with the oxygen molecule were derived from improved data in a preceding joint paper.[1] A new band, named A', was described and attributed to oxygen but no explanation was offered for it. In a recent paper Mulliken[2] has discussed the interpretation of the atmospheric bands, showing that they may be attributed to a transition from the normal ^3S state to a metastable ^1S excited state of the molecule, but he did not account for the A' band. Giauque and Johnston,[3] however, have pointed out that the A' band as described by Dieke and Babcock,[4] corresponds to one which would be expected if oxygen consists of two isotopes, one of mass 16 and another, much less abundant, of mass 18. Aston[5] finds with the mass spectrograph no evidence for O^{18} and concludes that if it exists its proportion can hardly exceed 1:1000 of O^{16}.

Further data confirming the existence of O^{18} are now presented and the proportions of O^{16} and O^{18} are found to be consistent with Aston's conclusion. In addition, some other new features of the band spectrum of oxygen are described, one of which indicates the existence in the ordinary molecule of something equivalent to a minute dissymmetry.

Table 1 gives a revised description of the A' band, following the notation of Dieke and Babcock. The band is now considerably extended in all branches and a few inadvertent errors in the previous description are corrected. An important change is the inclusion of the odd-numbered doublets with intensities similar to those of even number formerly given alone. Some of the added material was measured by us but omitted from our paper because we failed to recognize its connection with the band. On account of the dissymmetry of the molecule O^{16}–O^{18} the odd-numbered doublets should appear, and interpolation between the even-numbered doublets shows that the new lines do in fact coincide with their expected positions. The data of table 1 confirm the existence of O^{18}. Excepting the zero line of the P branch, which is a forbidden line, the vacant spaces in table 1 are due to obscuration by strong lines of the A band.

A comparison of the observed positions of the even-numbered doublets in the A' band with those calculated from the theory of the isotope effect in band spectra is summarized in table 2. The equations used are those stated by Giauque and Johnston as follows:

$$\Delta\nu(P) = 2.12 + 0.0556[B''m^2 - \beta''m^4 - B'(m-1)^2 + \beta'(m-1)^4]$$
$$\Delta\nu(R) = 2.12 + 0.0556[B''m^2 - \beta''m^4 - B'(m+1)^2 + \beta'(m+1)^4]$$

where $m = {}^3/_2, {}^7/_2, {}^{11}/_2 \ldots\ldots\ldots\ldots$ The constants are as found by Dieke and Babcock:

$$B'' = 1.438;\ B' = 1.390;\ \beta'' = 6.31 \times 10^{-6};\ \beta' = 5.75 \times 10^{-6}.$$

Only the residuals, observed *minus* computed wave number, are given in table 2, and those lines which occur in more than one place in the band are omitted, since their positions are less accurately determined. The average residual is -0.05 cm.$^{-1}$, and, as the signs are practically all negative, it is evident that there is a small systematic discrepancy between the observed and computed positions of the A' lines. This difference appears slightly greater than the estimated errors of observation, although it must be remembered that we are comparing positions of lines whose intensities are widely different and, in spite of numerous precautions, some unsuspected instrumental error may have entered. The residuals show no relation to the amount of rotational energy, and, if real, the systematic difference would appear to be associated with the vibrational

TABLE 1

A′ BAND

j	λ	INT. $P_1(j)$	VAC.	λ	INT. $P_2(j)$	VAC.
0	7619.691	00	13120.29	.....	...	.....
1	21.312	00	17.50	7620.064	00	13119.64
2	22.998	00	14.59	21.818	00	16.62
3	.....	...	.....	23.540	00	13.56
4	26.513	0	08.55	25.345	0	10.56
5	.....	...	.....	.....	...	.....
6	30.232	0	02.16	29.084	0	04.13
7	.....	...	.....	.....	...	.....
8	34.161	0	13095.42	33.028	0	13097.36
9	.....	...	.....	.....	...	.....
10	38.298	0	88.32	37.172	0	90.25
11	40.47	0	84.60	39.32	0	86.57
12	42.639	0	80.89	41.53	0	82.79
13	44.90	0	77.02	43.79	0	78.92
14	47.188	0	73.11	46.10	0	74.97
15	49.581	0	69.02	48.46	0	70.94
16	51.95	00	64.97	50.88	00	66.80
17	54.45	00	60.71	53.34	00	62.60
18	56.925	00+	56.48[b]	55.83	00	58.35
19	59.90	00 00	51.42[d]	58.42	00	53.94
20	62.10	000	47.67	61.05	0000	49.45
21	.....	...	.....	63.72	000	44.91
22	67.51	0000	38.46	66.49	0000	40.20
23	70.34	0000	33.65	69.22	0000	35.55
24	73.15	0000	28.88	72.05	0000	30.74

j	λ	INT. $R_1(j)$	VAC.	λ	INT. $R_2(j)$	VAC.
1	.....	...	.....	7615.55	0	13127.44[b]
2	7615.55	0	13127.42[b]	14.00	00	30.09
3	13.71	00	30.60[b]	12.57	0	32.55[b]
4	12.57	0	32.55[b]	11.188	0	34.94
5	11.002	0	35.26	09.84	00	37.26
6	09.71	00	37.49	08.55	{0 0}	39.49[b,d]
7	08.55	{0 0}	39.49[b,d]	07.358	1	41.55[b]
8	07.358	1	41.55[b]	06.211	{0 0}	43.54[b,d]
9	06.211	{0 0}	43.54[b,d]	05.07	0	45.50
10	05.194	0	45.29	04.004	0	47.35
11	04.2	0?	47.01	02.996	0	49.10
12	03.212	0	48.72[d]	02.028	00	50.77
13	.....	...	.....	01.12	0	52.34
14	01.38	0000	51.9	.....	...	.....
15	.....	...	.....	7599.45	0	55.23
16	.....	...	.....	.....	...	.....
17	7599.215	0	55.64	97.995	1	57.75[b]
18	.....	...	.....	.....	...	.....
19	97.995	1	57.75[b]	96.75	000	59.91
20	.....	...	.....	.....	...	.....
21	96.97	0000	59.53	95.58	00	61.93
22	.....	...	.....	94.28	0	64.18
23	.....	...	.....	.....	...	.....
24	.....	...	.....	93.84	0	64.95

[b] = used in more than one position in the bands.
[d] = double

part of the isotopic displacement. Since it amounts to less than 4 parts in a million, it can hardly be taken as a refutation or even a serious weakening of the arguments in favor of the existence of O^{18}. No other hypothetical isotopes of oxygen correspond to the observations.

An examination of the B band was made under favorable conditions in the hope of finding further evidence, although the isotopic band would be expected to appear less strongly here than in the case of the A band. The photographs show many new faint lines intermingled with the B band and some of these have the appearance of a new band with nearly the same displacement from B as that of A' with respect to A. But the isotopic displacement calculated for O^{16}—O^{18} is in this case very different, and no correspondence has yet been found between these new lines and those to be expected in a band truly analogous to A'. Further study of this material is in progress. It is clearly of atmospheric origin and probably arises from oxygen, but more accurate measurements are needed before it can profitably be discussed.

A summary of the evidence for the existence of O^{18} would include: (1) as shown by Dieke and Babcock, the A' band has the same origin as the A band; (2) the odd-numbered doublets are present in A' as required by the theory; (3) the observed positions of the A' lines closely correspond to those calculated from the theory when coefficients for the molecule O^{16}–O^{18} are used; (4) the theory is well confirmed in the case of other elements whose isotopes have been discovered and studied with the mass spectrograph.

Another feature of both the A and B bands consisting of a series of exceedingly weak doublets, which are recorded only with powerful spectrographs when the sun is near the horizon, has been brought out during the progress of this work. These are found symmetrically placed between the intense doublets of both the P and R branches. The new doublets are listed in table 3 along with the ordinary lines of these bands which are repeated from the paper of Dieke and Babcock. The intensities given for the strong lines are only qualitative. The weak lines here considered

TABLE 2

RESIDUALS, OBSERVED *minus* COMPUTED ISOTOPIC DISPLACEMENT OF A' BAND FROM A.
(UNIT, CM.$^{-1}$)

P_1	P_2	P_1	P_2	R_1	R_2
−0.03	....	−0.06	−0.06	....	−0.01
−0.05	−0.11	−0.06	−0.10	....	−0.04
−0.06	−0.04	−0.05	−0.04	+0.01	±0.00
−0.06	−0.03	−0.04	−0.08	−0.06	−0.07
−0.05	−0.03	−0.03	−0.10	−0.02	−0.06
−0.07	−0.04	−0.10	−0.04	....	....
−0.06	−0.04	....	....	....	....

are estimated to be about one-tenth as strong as the adjacent lines in the isotopic band and, as will be seen from what follows, this would correspond to about one ten-thousandth the intensity of the adjacent strong lines of the ordinary band. Comparison with the positions calculated for the missing doublets by means of the isotopic displacement and also by graphical interpolation between the strong doublets shows that the observed positions agree approximately but not exactly. The mean difference is -0.11 cm.$^{-1}$ with a range from $+0.58$ to -0.70 cm.$^{-1}$. The errors of observation, although considerably larger for these difficult lines, are not great enough to account for such differences. These doublets cannot be ascribed to a third isotope of oxygen[6] and there is no place for them in any of the bands already described except the one chosen. They cannot be explained as accidental coincidences, since there are too many of them in view of the fact that practically no other lines of similar character occur in this region. It seems probable that they are in fact the missing doublets, affected by some slight perturbation. The existence

TABLE 3

A BAND

j	λ	INT. $P_1(j)$	ν VAC.	λ	INT. $P_2(j)$	ν VAC.
0	7620.996	15	13118.04	.....	...	.....
1	22.50	0000	15.45	7622.02	0000	13116.28
2	24.493	23	12.02	23.289	22	14.11
3	26.17	0000	09.14	25.45	0000	10.38
4	28.203	25	05.64	27.050	24	07.63
5	30.01	000	02.54	29.19	000	03.97
6	32.150	25	13098.87	31.021	24	00.81
7	34.05	000	95.61	33.34	000	13096.82
8	36.317	25	91.72	35.196	24	93.64
9	38.298	0	88.32[d]	37.28	0000	90.07
10	40.694	23	84.22	39.583	22	86.12
11	42.77	0000	80.67	41.64	0000	82.60
12	45.297	19	76.34	44.197	18	78.22
13	47.43	0000	72.70	46.21	0000	74.78
14	50.120	16	68.10	49.032	15	69.96
15	52.39	0000	64.22	50.88	000	66.80[d]
16	55.172	13	59.47	54.078	12	61.34
17	.....	...	.....	56.925	00	56.48[b]
18	60.447	10	50.48	59.359	9	52.34
19	.....	...	.....	62.10	000	47.67[b]
20	65.938	6	41.13	64.873	6	42.95
		R_1			R_2	
1	7617.56	0000	13123.95	7617.08	0000	13124.78
2	16.143	10	26.40	15.048	17	28.28
3	14.55	00	29.14	13.77	0	30.49
4	13.180	19	31.51	12.054	23	33.45
5	11.63	000	34.18	11.002	0	35.26[b]
6	10.450	23	36.21	09.290	27	38.22
7	.....	...	.....	08.55	0	39.49[b,b]
8	07.911	24	40.60	06.748	27	42.61
9	.....	...	.....	.....	...	.....
10	05.628	24	44.54	04.431	24	46.61
11	.....	...	.....	03.28	0	48.60[b, b]
12	03.533	17	48.13	02.346	18	50.22
13	.....	...	.....	01.34	0000	51.95
	x	x	x	x	x	x
25	.....	...	....	7594.28	0	64.18

B BAND (NEW LINES ONLY)

		P_1			P_2	
3	6888.41	000	14513.14	6887.20	0000	14515.69
5	91.59	000	06.44	90.73	000	08.26
7	95.37	0000	14498.49	94.34	0000	00.66
9	98.92	000N	91.00	97.94	0000N	93.1[d]
11	6903.03	0000	82.40	.....	...	.....
13	06.98	000	74.12	.....	...	.....
15	11.91	000	63.80	.....	...	.....

of these doublets has hitherto been unrecognized, although Mulliken[7] says of them

> These might perhaps after all be expected in very low intensity, corresponding to some small interaction neglected in the ordinary theory, even in a homopolar molecule without nuclear spin.

The intensities of the absorption lines in the oxygen bands show a remarkable range. During this investigation the most persistent features of the A band were photographed with an air path of 3 meters with a spectrograph whose photographic resolving power is about 20,000. If an instrument of higher power but shorter air path were available, it seems probable that 1 meter of air would suffice to show the strongest lines in this band. In contrast with such lines we have the last observable members of the regular sequence of doublets, at λ 7717–7718, barely recorded by a spectrograph of about 10 times as great resolving power with an air path 30,000 times as great, and also the strongest of the missing doublets, of comparable intensity. Between these extremes lie the strongest lines of the isotopic band, A', whose intensities relative to those of the A band should give an estimate of the relative abundance of O^{16} and O^{18}.

The ratio of these intensities is too great to be measured satisfactorily by direct comparison. Eye estimates are meaningless and even the microphotometer proves inadequate. Fortunately a null method of great simplicity is available. The two bands, A and A', are successively recorded on portions of the same photographic plate which are given the same development. For the A band an artificial source of light is used with a measured air path of a few meters, while for A' the solar spectrum is observed with identical instrumental adjustments but with a much greater equivalent air path, which may be readily calculated from the height of the barometer, known density of air under the conditions of observation, and zenith distance of the sun at the given time. By proper choice of circumstances homologous members of the two bands are made to appear alike and their actual relative intensities may then be taken as the ratio of the two air paths. The method may be refined by applying the microphotometer to test the equality of the two sets of lines, but this was hardly justified in the present case since eye estimates are quite reliable when the differences are small. Two determinations gave respectively 1:1175 and 1:1350 as the ratio of A' to A, which may therefore be put equal on the average to 1:1250, the actual ratio of O^{18} to O^{16} atoms.

The magnitude of this ratio explains the fact that the isotope of oxygen has not been discovered in the usual way with the mass spectrograph, and is in agreement with the conclusion of Aston to which reference has already been made. It is interesting to note that the spectroscopic method has once before led to the discovery of an isotope when Mulliken[8] showed the

existence of Si^{30}, which was later confirmed by Aston[9] with the mass spectrograph. Other useful data on the relative intensities of lines in the atmospheric oxygen bands may be derived from photographs like those used in this investigation, but their discussion must be reserved for a future paper.

[1] Dieke and Babcock, these PROCEEDINGS, **13**, 1927 (670–678); *Mt. Wilson Comm.*, No. 101.

[2] Mulliken, *Phys. Rev.*, N. S., **32**, 1928 (880–887).

[3] Giauque and Johnston, *Nature*, **123**, 1929 (318).

[4] Dieke and Babcock, loc. cit.

[5] Aston, *Nature*, **123**, 1929 (488–489).

[6] *Note added in proof.*—In a letter soon to be published in *Nature*, Drs. Giauque and Johnston show that these weakest doublets in the *A* band correspond to a second isotopic molecule, O^{16}–O^{17}. I had examined the data with this point in view but an error in computation obscured the truth, and I was further misled by the approximate accordance noted in the text, as well as by the apparent repetition of the sequence of weak doublets in the *B* band, where the isotopic bands have not yet been shown to exist. Further study of my data has confirmed the conclusion of Giauque and Johnston.

[7] Mulliken, *Phys. Rev.*, N. S., **32**, 1928 (886).

[8] Mulliken, *Nature*, **113**, 1924 (423–424); **116**, 1925 (14); *Phys. Rev.*, N. S., **26**, 1925 (319–324).

[9] Aston, *Nature*, **114**, 1924 (273).

FOSSIL PLANTS AND MOUNTAIN UPLIFT IN THE PACIFIC STATES

BY EDWARD W. BERRY

DEPARTMENT OF GEOLOGY, JOHNS HOPKINS UNIVERSITY

Communicated May 9, 1929

Through force of circumstances I have been compelled to devote considerable time during the past few years to extensive Miocene floras that have come to light, especially in eastern Washington and Idaho. The time spent has not been altogether unprofitable because of the bearing of these floras on the geologic history of the West—especially the time of uplift of the Sierra Nevada and Cascade ranges, on the distribution of terrestrial plants, and on the progressive provincialism of the North American flora, which last only reached its culmination in post-glacial times.

A preliminary statement of results has just been published as Professional Paper 154H by the U. S. Geological Survey. This deals with the fossil flora of a restricted area at or near Spokane, Washington. The present note is intended to call attention to some general conclusions

growing out of this and of other uncompleted studies which will not be finished for several years.

Geologists who have studied the Spokane area[1] describe a thick series, possibly as much as 1500 feet in thickness, of mostly diatomaceous lacustrine clays with subordinate amounts of sand and gravel, which they explain as due to the damming of the Miocene drainage by the successive sheets of the so-called Columbia lavas which advanced from the west.

Consequently if the age of these lake beds can be determined it will afford some measure of the age of the Columbia lavas. Unfortunately this age cannot be precisely determined as yet, but the recent studies of the flora contained in these lake beds show that they are somewhat younger than has previously been supposed. They cannot be older than middle Miocene and they are probably of upper Miocene age, although this determination still awaits conclusive proof.

The flora from the lake beds at Spokane, which is described in the publication previously mentioned, amounts to slightly more than 150 species, and is exceeded in size among western Miocene floras by only the classic locality at Florissant, Colorado, and the Spokane plants are not only more abundant, but are better preserved than those from Florissant. New forms are continually encountered and several of great interest have been determined and described since the manuscript of the report, of which this note is somewhat in the nature of an abstract, went to press.

An enumeration of a few of the plants represented will give a sufficiently accurate idea for our present purposes of the climate under which they flourished: 3 mosses, a lycopodium, an equisetum, 4 ferns, Sequoia, Taxodium, Typha, Potamogeton, Smilax, Hicoria, Salix, many poplars, maples, oaks, chestnuts, birches, alders and elms, Platanus, Magnolia, Liriodendron, Liquidambar, Tilia, Sassafras, Cercis, Nyssa, Diospyros, etc. At least a dozen of the few mentioned are no longer represented in western North America but have survived in either southeastern Asia or southeastern North America, or in both of these regions. Of the majority of those which have maintained themselves west of the Rocky Mountains to present times their ranges have become greatly restricted since the Miocene.

Without taking the space to prove my conclusions, I think that the foregoing list is sufficient to show that this fossil flora was overwhelmingly mesophytic, and demanded a climatic environment essentially like that of the present area of mixed hardwood forests of southeastern North America. It could not live at the present time in the vicinity of Spokane because the precipitation is not only actually deficient, but what does fall is largely at the wrong season of the year for plant growth.

The major factors in the present-day climate of the western United

States are the direction of the prevailing winds and the character of the topography. If attention is confined to the state of Washington it may be noted that these lake beds lie in the present transition zone between the treeless Sonoran arid zone which occupies so much of the Great Basin and the, in general, forested Canadian zone of western Washington between the Cascades and the coast, and of the mountains both to the north and the east. The Pacific facing slopes of the Cascades, over a 24-year period have shown a mean annual precipitation over four times that recorded at Spokane, and as the Puget region is approached this may increase to five times that at Spokane.

Again, without taking the space to discuss the subject in any detail, it is clear that the major factor in bringing about the present distribution of the floras of the Pacific states and the extensive post Miocene extinctions and restrictions of range, has been the elevation of the mountains across the paths of the prevailing moisture-carrying winds. This gives us a method of dating, at least approximately, the elevation of the mountains, and this method becomes precise pari passu as the floral record becomes more complete and more precisely dated.

As applied to the state of Washington the Cascades could not have been sufficiently elevated at the time the fossil flora flourished at Spokane to have interfered with an abundant supply of moisture. Hence their main elevation was at some subsequent time. If the flora can be shown to be upper Miocene, as I believe will eventually prove to be the case, then this elevation could not have been earlier than very late Miocene or at some time during the Pliocene or Pleistocene. If my present belief should turn out to be incorrect and this flora should subsequently be proved to be middle Miocene, then the main elevation may have taken place at any time between the upper Miocene and the present.

This method can only be applied in the case of mountain ranges transverse to prevailing winds which hence bring about contrasted conditions on the two sides, and then it only fixes the date before which elevation could not have taken place and does not give the actual date when it did take place. If the mountains rise to very lofty heights, particularly in the equatorial zone so that various altitudinal climatic zones can be differentiated, as in the Central and Northern Andes, it may then be possible, if the fossil record is not too incomplete, to secure data as to the approximate amount of elevation.

The present status of the investigation shows that not only the Cascades but the Sierra Nevada as well, were elevated in the very late Tertiary.

Turning now to the progressive provincialism of the floras of western North America, there is space for but a brief statement. During the Miocene the Pacific slope was largely clothed with a mesophytic forest of mixed hardwoods with a considerable admixture of conifers. The

facies of this flora is scarcely distinguishable from those of contemporaneous age in eastern North America, or Europe, and if we can judge from very limited information, those of a considerable part of temperate Asia. Certainly such a statement is quite as accurate and as fully justified as that of the holarctic range of the so-called Hipparion terrestrial fauna of the late Tertiary.

This Miocene holarctic flora includes Ginkgo, Glyptostrobus, Sequoia, Taxodium, and Pinus among the gymnosperms, and a long list of dicotyledonous genera among the Angiosperms. Elements found in our West and not known to have been holarctic, such as Tumion and Libocedrus together with a number of angiosperms, had a much wider range than today. Most of the more widely distributed genera, such as Sequoia, Taxodium, Magnolia, Hicoria, Sassafras, Nyssa, Glyptostrobus, etc., became extinct in Europe during the Pleistocene glaciations, but survived in China and southeastern North America. A few of the western Miocene trees survived in that region in favorable situations to which they subsequently became restricted. Among these are the redwood of the wet coastal valleys, the big trees of the fog belt of the western slopes of the Sierra Nevada; the incense cedar (Libocedrus) which continues in small groves on the western slopes of the Cascades, Sierra Nevada and coast ranges; the sycamore (Platanus), Cercis, Juglans and horse chestnut (Aesculus) which have survived in limited areas along streams in California.

Among those that failed to adapt themselves to the climatic changes following mountain uplift in the West, or to maintain themselves in relict environments, were Miocene representatives of the genera Comptonia, Liriodendron, Castanea, Hicoria, Fagus, Ulmus, Carpinus, Magnolia, Liquidambar, Hydrangea, Celastrus, Tilia, Sassafras, Nyssa, Paliurus, Amygdalus, etc. The last two, along with Ginkgo and Glyptostrobus, disappeared altogether from North America, but survived in Asia; the balance all survived in eastern Asia and eastern North America. Thus their surviving descendants are separated from their Miocene occurrences in Washington, Idaho, Oregon, Nevada and California by the breadth of the Pacific Ocean on the west and the broad belt of arid and prairie country on the east.

[1] Pardee, J. T., and Kirk Bryan, *U. S. Geol. Survey*, Prof. Paper **140**, pp. 1–16, 1926.

THE ANALYSIS OF A CONCRETE CASE OF INTERGRADATION BETWEEN TWO SUBSPECIES. II. ADDITIONAL DATA AND INTERPRETATIONS[1]

BY FRANCIS B. SUMNER

SCRIPPS INSTITUTION OF OCEANOGRAPHY, UNIVERSITY OF CALIFORNIA

Communicated April 22, 1929

In a recent number of these PROCEEDINGS[2] I presented some of the more important results of an intensive study of intergradation between two subspecies of *Peromyscus*. It was my announced intention to follow that article by a more extended one, to be published elsewhere, and covering in part the same ground. Since, however, such a procedure would involve much needless repetition, both of text and figures, it seems preferable that the earlier paper should merely be supplemented by another brief one, containing the more important additional material. Under the circumstances, an understanding of the present paper presupposes some knowledge of the earlier one.

In the following pages are included (1) a map, showing the actual spatial relations of the various trapping "stations;" (2) a half-tone illustration, representing average specimens of the seven local populations here considered; (3) a table, giving the mean values and standard deviations for all of the characters measured, including some which were not mentioned in the previous report; (4) a discussion of correlation, both intra-racial and inter-racial; (5) a more extended discussion of various theoretical questions involved in an endeavor to interpret this situation.

The position of the collecting stations (Fig. 1) was not chosen arbitrarily, as might be inferred from their irregular distribution. It was determined to some extent by agricultural conditions, but chiefly by the ascertained nature of the populations at various points. Thus after trapping near Chipley and Round Lake, at points only ten miles apart, it became evident that intensive collecting was necessary between these stations. On the other hand, it was not thought worth while to make collections between Graceville and Abbeville, a distance of nearly fifty miles, owing to the close similarity of these two populations.

The picture presented by the series of pelages (Fig. 2) may be profitably compared with the histograms comprised in figure 1 of the February paper, and with the values given in the table below.

The racial differences among the various characters shown in table 1 have, for the most part, been portrayed graphically in the previous paper. But certain other mean values, absolute and relative, deserve consideration here. Three of these have been plotted in figure 3 of the present paper.

FIGURE 1

Map of area considered in present paper. Squares represent sections of land in which trapping was conducted. (In most cases, the actual township and section were ascertained, and the position of the latter has been correctly indicated on the map.)

Areas heavily shaded represent the major stations, upon which the present discussion is almost entirely based; those lightly shaded are the minor ones. Results from the latter stations are in complete harmony with the others, so far as they go.

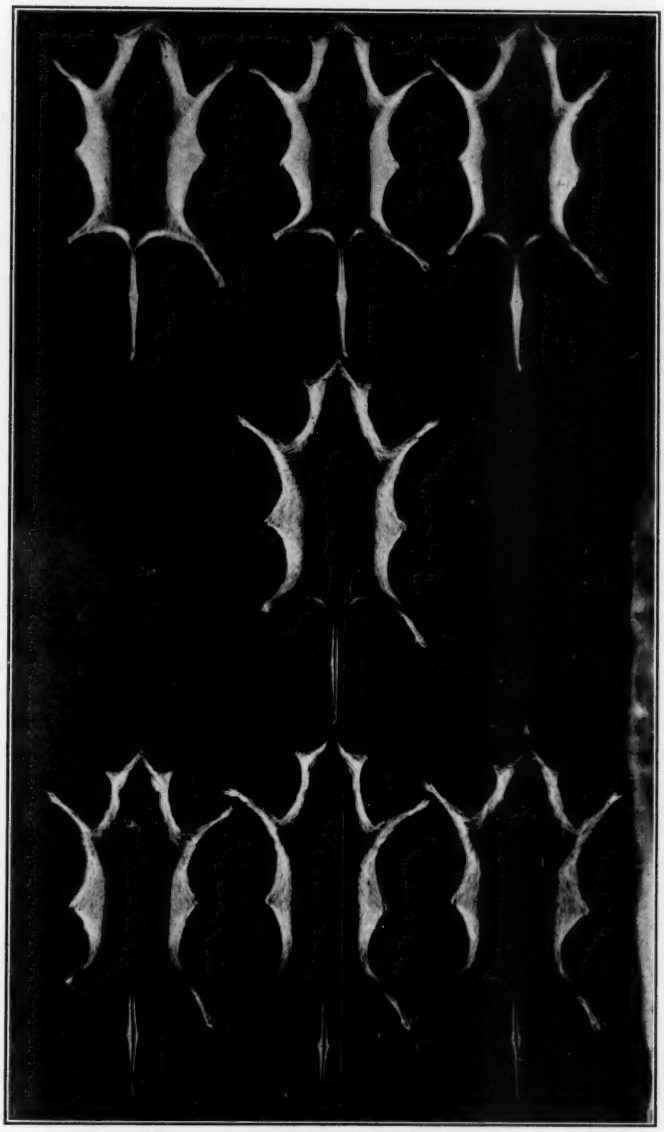


FIGURE 2

Photographs of a series of skins, representing the seven chief local populations here considered. The specimen chosen, in each case, stands close to the average in respect to the values of "colored area," "red," and the "index of saturation." 1, Shore; 2, Crystal Lake; 3, Round Lake; 4, Intergrades; 5, Chipley; 6, Graceville; 7, Abbeville.

Foot pigmentation denotes the depth of pigmentation of the foot, graded according to an arbitrary scale.[3] It will be seen that the mean values for this character present nearly the same relations as those shown by the other pigmental characters in figure 3 of the February article. The single exception is the value for the Graceville collection, which is considerably lower than would have been expected.

$\frac{Ca}{R}$ is the value obtained by dividing the measurement for "colored area" by that for "red." Since the latter figure is used here as an index of the paleness or darkness of the dorsal region of the pelage (a high value denoting a pale pelage, and vice-versa), this fraction is roughly indicative of the total amount of pigment present. The "curve" for this fraction presents the same peculiarities as those for the other pigmental characters. The range of variability among these local races, in respect to this value, is naturally greater on the whole than that shown by either of the characters upon which it is based, taken singly.[4]

$\frac{R - V}{R}$ may be regarded as an "index of saturation," as regards red.[5] High values of this fraction indicate a relatively rich coloration, low values an approach to neutral gray. Disregarding the collection from the white sand dunes of the coast, it is seen that the pelages are progressively grayer as we proceed inland. The low saturation of the color of the coast-dwelling specimens is due to the greater proportion of white hairs in their fur. In this case, therefore, low saturation is associated with high luminosity, while in the case of the dark interior race (*polionotus*) low saturation is associated with low luminosity.

Our present discussion of *correlation* will be confined to pigmental characters. In the earlier section of this report, it was shown that the only characters displaying any consistent trend in their geographic variation were those relating to pigmentation. It is hence a matter of considerable interest to determine the extent of the correlations, both intra-racial and inter-racial, which are shown among these various characters. To what extent, if any, do these characters tend to vary together within a single local population, and to what extent do they tend to vary together, as we pass from one locality to another?

The correlation between the extent of the colored area of the pelage and the depth of pigmentation of the foot is found to be slight or wanting within each of the seven local populations here considered. Five of these correlations are positive and two are negative, the weighted mean of the seven coefficients being $+0.099$.[6]

On the other hand, these same two characters are found to vary together markedly as we pass along our geographic gradient from the coast inland. When we view these races in succession, we find that the mean area of the

TABLE I

NUMBER OF INDIVIDUALS	SEX	ALBIFRONS (COAST) 51		ALBIFRONS (CRYSTAL LAKE) 58		ALBIFRONS (ROUND LAKE) 54		POLIONOTUS-ALBIFRONS INTERGRADES 43	
		MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ
Body length (head + trunk)	♂	78.27 ± 0.24	1.67	76.12 ± 0.22	1.66	76.38 ± 0.22	1.78	77.22 ± 0.35	2.52
Body length (head + trunk)	♀	82.83 ± 0.28	2.21	82.11 ± 0.35	2.90	80.96 ± 0.42	3.02	82.78 ± 0.34	2.27
Body length (head + trunk)	Both	80.86 ± 0.28	3.02	79.42 ± 0.34	3.84	78.42 ± 0.30	3.32	79.80 ± 0.38	3.67
Tail length (actual)	Both	55.67 ± 0.23	2.40	49.66 ± 0.24	2.71	49.02 ± 0.23	2.47	50.30 ± 0.26	2.52
Tail length (corrected)*	Both	55.41		49.93		49.60		50.37	
Foot length (actual)	♂	18.35 ± 0.05	0.33	16.78 ± 0.06	0.48	17.02 ± 0.06	0.46	17.37 ± 0.07	0.55
Foot length (actual)	♀	18.26 ± 0.06	0.46	17.03 ± 0.05	0.38	16.82 ± 0.06	0.42	17.37 ± 0.06	0.40
Foot length (corrected)*	♂	18.37		17.45		17.27		17.68	
Foot length (corrected)	♀	18.02		16.85		16.79		17.43	
Ear length (actual)	Both	15.53 ± 0.04	0.44	14.41 ± 0.04	0.46	14.37 ± 0.04	0.44	15.20 ± 0.06	0.55
Tail stripe length**	Both	16.14		17.61		44.67		88.73	
Foot pigmentation	Both	0.20 ± 0.04	0.44	0.55 ± 0.06	0.60	1.00 ± 0.08	0.81	1.58 ± 0.07	0.65
Colored area of pelage†	Both	56.69 ± 0.61	6.50	61.66 ± 0.36	3.82	66.16 ± 0.40	4.29	71.10 ± 0.57	5.52
Pigmentation of ventral hair	Both	0.00		0.04		0.20		1.77	
Red	Both	18.15 ± 0.14	1.43	17.35 ± 0.15	1.55	15.74 ± 0.14	1.54	11.80 ± 0.22	2.08
$\frac{Ca}{R \cdot}$	Both	3.15 ± 0.05	0.51	3.59 ± 0.04	0.44	4.26 ± 0.06	0.65	6.27 ± 0.15	1.48
$\frac{R - V}{R}$ ‡	Both	37.34 ± 0.53	5.52	41.86 ± 0.40	4.22	37.88 ± 0.45	4.82	36.69 ± 0.63	6.02

TABLE I (*Continued*)

NUMBER OF INDIVIDUALS	SEX	POLIONOTUS (CHIPLEY) 58		POLIONOTUS (GRACEVILLE) 53		POLIONOTUS (ABBEVILLE) 60		MINOR COLLECTIONS ALBIF. (GAINER) 3	ALBIF. (COMPASS L) 1	POLION. (M. L. DEKLE) 22
		MEAN	σ	MEAN	σ	MEAN	σ	MEAN	MEAN	MEAN
Body length (head + trunk)	♂	76.37 ±0.26	2.00	78.84 ±0.20	1.58	78.16 ±0.31	2.55	77.50	74.00	78.45
Body length (head + trunk)	♀	82.81 ±0.36	3.04	83.38 ±0.44	3.28	83.34 ±0.36	2.89	82.50		81.55
Body length (head + trunk)	Both	79.92 ±0.37	4.14	80.98 ±0.31	3.40	80.67 ±0.33	3.75	80.83		80.00
Tail length (actual)	Both	50.71 ±0.25	2.75	50.10 ±0.25	2.66	51.00 ±0.22	2.54	46.83	50.50	49.52
Tail length (corrected)*	Both	50.74		49.70		50.66				
Foot length (actual)	♂	17.29 ±0.06	0.48	17.46 ±0.06	0.45	17.32 ±0.07	0.56	17.30	16.70	17.25
Foot length (actual)	♀	17.52 ±0.05	0.40	17.39 ±0.06	0.41	17.43 ±0.06	0.46	16.60		17.11
Foot length (corrected)*	♂	17.51		17.61		17.53				17.38
Foot length (corrected)	♀	17.38		17.21		17.08				17.03
Ear length (actual)	Both	15.21 ±0.05	0.51	15.26 ±0.05	0.53	15.12 ±0.04	0.50	14.97	14.00	14.92
Tail stripe length**	Both	98.02		100.00		100.00		13.70	66.67	100.00
Foot pigmentation	Both	1.80 ±0.06	0.65	1.47 ±0.07	0.72	2.02 ±0.06	0.70	0.00	0.00	1.64
Colored area of pelage†	Both	74.51 ±0.29	3.15	76.63 ±0.24	2.51	77.22 ±0.24	2.78	62.33	69.00	75.27
Pigmentation of ventral hair	Both	1.96		2.00		2.00		0.00	0.00	1.86
Red	Both	10.43 ±0.10	1.08	9.67 ±0.10	1.11	9.99 ±0.10	1.13	16.47	15.00	11.10
$\frac{Ca}{R}$	Both	7.22 ±0.08	0.85	8.03 ±0.09	0.99	7.83 ±0.08	0.96			6.89
$\frac{R - V}{R}$ ‡	Both	32.81 ±0.38	4.19	32.02 ±0.40	4.24	30.13 ±0.42	4.78			31.55

* Probable values for a standard body length of 80 mm.

** Expressed as percentage of length of exposed part of tail.

† In this case the area of hair which is pigmented throughout its entire length.

‡ V designates "blue violet" (designated BV in *J. Mammalogy*, 1927).

colored part of the pelage increases steadily, there being no exception to this (February paper, figure 1). Likewise, the mean depth of foot pigmentation increases steadily, with a single exceptional case (present paper, figure 3).

When these seven local collections are thrown together, and treated statistically as a single population, the correlation between the last-named pair of characters is found to be $+0.613$, this figure being based upon 358 individuals.[7]

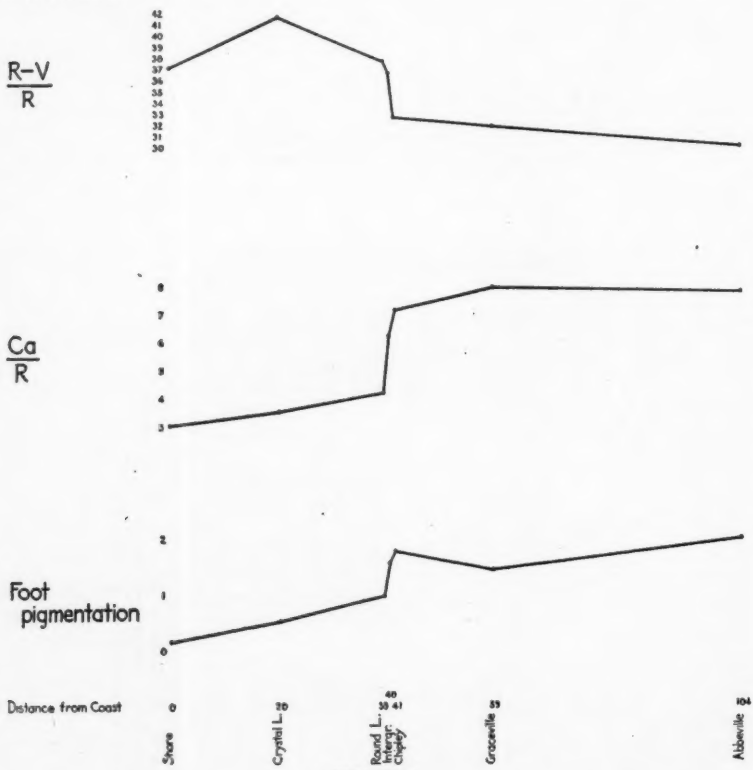


FIGURE 3

Graphs, based upon average values for foot pigmentation, Ca/R, and $\frac{R}{R-V}$.

Certain other correlations between pigmental characters deserve mention here. As regards the correlation between foot pigmentation and red, we find that in six cases out of seven the coefficient is negative, the weighted mean being -0.129. When, on the other hand, we treat our entire material as a single population, this correlation rises to -0.643.[8]

Previous studies which I have made of other species of *Peromyscus* have revealed these same relations, as regards the two characters here considered, viz.: (1) darker races, as a rule, have darker feet; (2) within each separate race, there is little or no correlation between the pigmentation of the feet and that of the pelage.[9]

Considering finally the correlation between red and pigmented area, the mean of the intra-racial coefficients (all negative) is -0.363; that based upon the combined populations (357 individuals) being -0.864.

How are we to explain this coexistence of a high inter-racial and a low (or non-existent) intra-racial correlation between these same characters? In some previous discussions of the subject, I adopted the hypothesis that the two characters in question must have undergone simultaneous but independent genetic change, through the influence of some environmental agency. Such a conclusion would be inevitable if it were really true that the characters in question were not at all (or only slightly) bound together genetically within the organism, in such a way that an alteration of one would necessarily entail an alteration of the other. But, in reaching this earlier conclusion, I failed to recognize the fact that little or no correlation might be detected between the measurements of two characters in a given population, even in cases where these two characters were dependent upon absolutely identical genetic factors.

It is evident that the variations within a single population, upon which intra-racial correlations depend, cannot be altogether comparable with the variations which have led to the evolution of one race from another. There are strong reasons for believing that the former are to a considerable extent of the nature of "somatic modifications," which may affect various regions of the body, quite independently of one another, whereas the latter must of necessity depend upon "mutations," or hereditary variations, by whatever name these may be called.

That a considerable fraction of the intra-racial variability in pigmentation, here measured, is due to non-genetic causes is shown by the relatively low coefficients (averaging about 0.3) denoting parent-offspring correlation with respect to these characters. On the other hand, the fixity of the inter-racial differences, under changed conditions of environment, is evidence that these latter differences are mainly, if not wholly, of the genetic order.

It seems certain, in other words, that the difference between an average *polionotus* and an average *albifrons* is to a much greater extent dependent upon genetic factors than is the difference between a pale and a dark *polionotus* or between a pale and a dark *albifrons*.

The fact that we obtain low correlations, within our local races, in respect to various pigmental characters, is in no way inconsistent, therefore, with the supposition that these characters depend very largely upon the same

genetic factors, or at least upon closely linked factors. As additional evidence in favor of this supposition may be cited the marked increase which we frequently encounter in the correlation between any two pigmental characters, in the F_2 hybrid generation, and in back-crosses, as compared with F_1 hybrids and pure races.[10] It is hardly necessary to point out that no such an increase in correlation in the F_2 generation would follow automatically from the increase of variability in both of these characters, which occurs in the F_2 generation, as compared with the F_1. It results from the circumstance that the variability of the "segregating" generations is due more largely to genetic differences than is that of first crosses.

If the foregoing reasoning is correct, it is evident that selection with reference to one of these pigmental characters—say, coat color—would be certain to involve ultimately the modification of any other—say, foot pigmentation—even though these two characters were found to be feebly, if at all correlated within particular local populations.

This renders superfluous the alternative hypothesis earlier adopted by me, namely, that these various characters have undergone simultaneous and independent genetic change under the influence of some environmental agency. The existence of such a process of parallel modification is here inferential, whereas the known facts discussed above are demonstrably competent to produce the results in question.

The foregoing discussion of correlation was written substantially as here presented before I became aware of the similar treatment by Bubnoff[11] of the problem last considered. This author found that certain characters of the shells of fossil ammonites were distinctly correlated when groups of closely related species were compared. He thereupon put to test the question "whether also this correlation exists among all the individuals of one species," finding that "measurement gave the surprising, but undoubted, result that within the variants of a species this correlation is not present, that each character varies by itself and is not necessarily bound up with corresponding alterations of another." (p. 165, translated.)

Bubnoff's interpretation of these facts appears to be identical with my own, namely, that the variations which distinguish these related species are "genotypic" alterations of form, while those which appear within the various species are somatic modifications ("zufällige Variante," in his words) and do not involve correlative changes. It is contrary to all analogy, however, to suppose that intra-specific differences in these characters of the shells of ammonites are wholly of the non-genetic sort. Nor does it seem probable that Bubnoff has found here a satisfactory criterion for separating species.[12]

In my previous communication upon this series of animals, certain

fundamental theoretical questions were reserved for later consideration. While any discussion of these questions must at the present time be largely speculative, I believe that we are already in possession of sufficient facts to warrant a preliminary effort in this direction. Indeed, there would be little incentive for engaging in such detailed observations and descriptions, if we were debarred from the possibility of attempting these interpretations.

Two chief problems present themselves in reference to the phenomena which have been discussed in these papers. (1) How did these races of mice become differentiated from one another? (2) How are we to explain the curious relations which we encounter in their geographic distribution? These questions may be considered in the order given.

Notwithstanding my earlier arguments for a more direct effect of environment in evolution (these I still regard as valid in certain cases) I will concede that the facts in the present instance seem to lend themselves better to an explanation based upon the selection of germinal variations which, in their origin, bore no specific relation to factors of the environment. I have already indicated my belief that the pale race *albifrons* arose from a dark race, similar to or identical with, the present *polionotus*. The most plausible explanation of these color changes, I think, is that we have to do with protective coloration, achieved through the differential survival of paler variants.

It is easy to discern, within every geographic race in nature, the small hereditary differences, through the accumulation of which one race may have been derived from another. Each such race presents a wide range of variability in respect to every character which has been measured, while it is experimentally demonstrable that these individual differences are in part genetic. Given an adequate basis for selection, tending to accumulate the differences in one direction or the other, it is easy to imagine how the divergence may have occurred.

It cannot, of course, be proved that any *new* germinal changes have occurred during the entire process by which these local races have become differentiated from one another. According to the currently accepted interpretation of selection, even such striking divergence as was obtained by Castle, with his hooded rats, resulted from a simple process of sorting-over of existing genetic materials. It is not at all impossible that genetic factors adequate for the production of *albifrons*, and even of the more extreme form, *leucocephalus*, were already present in the original *polionotus* stock. On the other hand, the occurrence of one highly aberrant individual[13] which falls within the limits of *leucocephalus*, in respect to extensity of color pattern, suggests that this sorting process may be supplemented by occasional mutations, i.e., actual changes in genetic factors.

Before leaving this subject, however, I wish to disclaim the belief that

all organic diversity is the result of selection, based upon utility. Much of it probably is; much of it, no less probably, is not.

It must here be recalled that none of the subspecific differences in *Peromyscus*, so far as these have been investigated, have been found to depend upon single Mendelian factors.[14] If the Mendelian scheme is really of universal application, we have to do with numbers of independently segregating factors, affecting each character. This, although the characters themselves, as stated above, may be closely correlated. The divergence of the races has been due, in every case, to the accumulation of small genetic differences; never to large abrupt changes or "saltations."

The facts cited in the foregoing paragraph lead us directly to the second of the two questions set forth above: How are we to explain the curious relations which we encounter in the geographic distribution of *polionotus* and *albifrons*? We have just seen that the latter race could not have arisen from the former by a single act of mutation. Thus the fairly abrupt transition between one race and the other, geographically speaking, can receive no such simple interpretation.

Among the curious relations here referred to there are two which deserve particular attention. One is the fact that such a highly depigmented condition should occur so far inland where there are no white beaches or dunes, at least ones which are exposed to view at the present time, and where the ground is largely covered by vegetation. The other is the fact that the boundary between the ranges of these two subspecies is as sharp as it is, despite their mutual fertility.

As regards the first of these problems, an appeal might be made to ecological conditions which have long ceased to exist. Perhaps at the time when *albifrons* was differentiating from *polionotus* there was much less top-soil and vegetation throughout this entire region, thus leaving the underlying pale sand more fully exposed to view. Or possibly the evolution of this race dates back to a time when the coast line, with its rampart of glistening white sand, lay considerable farther inland than at present. Unfortunately, such geological evidence as is available does not favor this supposition.[15]

On the other hand, it is possible that a fuller knowledge of the habits of these mice would reveal the need of their harmonizing with backgrounds of pale sand, even in territories where most of the soil is covered by vegetation. In support of such a contention, certain facts may indeed be cited: (1) the exposed soil of almost the entire *albifrons* zone, so far as my observations go, is sandy, and the sand, while mostly far from white, is distinctly pale, as compared with the soil somewhat farther north; and (2) the burrows of these mice appear to be nearly always located in patches of bare soil, while areas covered densely with weeds are distinctly unfavorable places for trapping them. Thus the need for concealing

coloration might be greater than would at first be suspected. However, even this supposition would not account for the extreme depigmentation of *albifrons*, a process which has been carried farther than in any except a few of our most highly modified desert types.

Viewing all the available evidence, it seems more likely that the entire differentiation of *albifrons* from its *polionotus*-like ancestor occurred upon the present gulf shore, where these animals abound upon areas of intensely white sand, largely uncovered by vegetation. Here the new race may have found an optimum habitat[16] and multiplied rapidly in consequence. This region may be supposed to have become, accordingly, a new "center of distribution" from which the expanding population pressed inland, displacing and absorbing the darker form, *polionotus*, until its advance was halted by the centrifugal pressure of the latter. The width of the zone occupied by the new race would depend upon the relative rates of multiplication of the two populations. This interpretation is essentially that offered by Grinnell, in his account of the origin of the chestnut-backed chickadee.[17] While it is, in the present instance, purely hypothetical, it seems to meet with fewer difficulties than any of the alternative explanations here considered.

But there is one highly important element in the situation which still remains to be accounted for. This is the fact which has previously been emphasized, that the transition between these two subspecies is at present so abrupt. One obvious explanation has already been rejected, namely, that our two races became differentiated in localities more remote from one another, and that they subsequently (and rather recently) came into contact. Aside from the utter lack of evidence for such a past geographic relation, is the presumable present contact of these two races, along a wide front, and the known existence of numerous similar cases elsewhere. These circumstances make it unlikely that we chance to be witnessing the first meeting of two previously separated populations.

In order to account for the lack of a more abundant intermediate population in our transitional area, we seem driven to one or both of two assumptions. These are (1) that there is a high degree of assortative mating, within each subspecies, and (2) that the intermediate or hybrid individuals are less viable *in either environment* than are the "pure" types.

Granted the operation of one or both of the above principles, it still remains unexplained why these races should not freely invade one another's territory, even if they do not intermingle genetically. We may dismiss at once the suggestion that there exists here some intangible ecological barrier, despite the apparent lack of one. For it seems quite improbable that a barrier rigid enough to produce such a sharp delimitation of races would entirely escape notice.

Nor would even a conspicuous and well-defined difference in soil color on the two sides of this subspecific boundary line be sufficient to bring

about such a hiatus. It happens that in passing from south to north we actually encounter in this vicinity a transition from paler to darker soils, representing a difference in the respective geological formations.[18] But there appears to be no close correspondence between the geological boundaries and the "peromyscological" ones, and in any case there is abundant evidence that selective elimination, on the basis of concealing coloration, is far from intense among these animals.[19] The discrimination on the part of their enemies would need to be well-nigh absolute in order to maintain a condition such as we actually find here.

It must be confessed that the causes responsible for the abrupt transition between the ranges of *polionotus* and *albifrons* are at present obscure. It is difficult to see how the mutual pressure of two expanding populations would, in itself, suffice to maintain a boundary at all sharp, where they came into contact. Careful field studies might reveal the existence of "social" or "psychical" factors, analogous to those which keep apart the races of mankind.

One question which is sometimes raised is whether the "intergrading" forms between two subspecies represent transitional stages in the evolution of one subspecies from the other, or whether they represent hybrids between the two after their differentiation has been accomplished. This question appears to me to be rather academic. If one of the races is still in the process of differentiating from the other, the "intergrading" forms will necessarily represent, in part, transitional stages. On the other hand, interbreeding doubtless occurs between the two races, both during and after their differentiation from one another, and thus part of the population will be of hybrid origin in any case. A little reflection shows that, genetically, there would be no necessary difference between such "hybrids" of the nth generation and individuals representing the various factorial combinations which would occur during the evolution of one geographic race from another.

Supplementary Note.—The foregoing paper had gone to press before I received the highly interesting article by W. Meise (Rassenkreuzungen an den Arealgrenzen, *Verh. d. deutschen zoöl. Gesellsch.* 32, Jahresvers., 1928, 96–104). Considerable parallelism will be noted between the two articles as regards both the problems discussed and the points of view of the two authors.

[1] These studies were conducted under the joint auspices of the Scripps Institution of Oceanography and the Carnegie Institution of Washington.

[2] Vol. **15,** no. 2, Feb., 1929.

[3] Sumner. *J. Exp. Zoöl.*, **30,** 1920, 402; *J. Mammalogy,* **8,** 1927, 185.

[4] This is because we are virtually dealing with a third power. *Ca* (which is an area) is multiplied by $1/R$. The *depth* of pigmentation (in one sense, at least) varies inversely with the value of R.

[5] Sumner, *J. Mammalogy,* **8,** 1927, 177–206.

[6] One of the minor collections, containing 22 specimens, gives a coefficient −0.046.

[7] A method of computing correlations in such aggregate populations, without the labor of calculating a new set of deviations, product moments, etc., has been developed by my colleague, Dr. G. F. McEwen. The formula, which is derived directly from that for the correlation coefficient, with corrections for approximate means, is as follows:

$$r = \frac{\Sigma(x_1y_1) + n_1(m_{x1} - m_x)(m_{y1} - m_y) + \Sigma(x_2y_2) + n_2(m_{x2} - m_x)(m_{y2} - m_y) + \dots}{n\left[\sqrt{\frac{n_1(\sigma_{x_1}^2 + (m_{x1} - m_x)^2) + n_2(\sigma_{x_2}^2 + (m_{x2} - m_x)^2) + \dots}{n}}\right] \times \left[\sqrt{\frac{n_1(\sigma_{y_1}^2 + (m_{y1} - m_y)^2) + n_2(\sigma_{y_2}^2 + (m_{y2} - m_y)^2) + \dots}{n}}\right]}$$

in which the subscripts 1, 2, etc., are attached to values for the various single local populations, while the corresponding values, without subscripts, are those for the aggregate population. This formula reduces to:

$$r = \frac{n_1r_1\sigma_{x1}\sigma_{y1} + n_2r_2\sigma_{x2}\sigma_{y2} + \dots + n_1a_1b_1 + n_2a_2b_2 + \dots}{[\sqrt{n_1\sigma_{x1}^2 + n_2\sigma_{x2}^2 + \dots + n_1a_1^2 + n_2a_2^2 + \dots}] \times [\sqrt{n_1\sigma_{y1}^2 + n_2\sigma_{y2}^2 + \dots + n_1a_1^2 + n_2a_2^2 + \dots}]}$$

in which a_1, etc., $= m_{x1} - m_x$, etc., and b_1, etc., $= m_{y1} - m_y$, etc.

[8] It is obvious that the correlation should be negative in the case of these two characters, since high values for "red" denote low degrees of pigmentation, and vice-versa.

[9] Sumner, *Ecology*, **6**, 1925, 365, 366.

[10] Huestis, R. R., *J. Exp. Zoöl.*, **41**, 1925, 464; Sumner and Huestis, *Biol. Bull.*, **48**, 1925, 51. Extensive evidence of this sort will be presented in a subsequent paper, dealing with the results of hybridization experiments.

[11] Bubnoff, S. von, *Zeitschr. indukt. Abst. Vererbungslehre*, **21**, 1919, 158–168.

[12] Dürken, B., *Ibid.*, **27**, 1922, 27–47.

[13] February paper, figure 1, lower left.

[14] Sumner, *J. Exp. Zoöl.*, **38**, 1923, 245–292; Huestis, R. R., *Ibid.*, **41**, 1925, 429–470.

[15] This I learn from Dr. C. Wythe Cooke, of the U. S. Geological Survey.

[16] This and certain other subspecies are found largely in association with the "beach oats" (*Uniola paniculata*) which presumably serves them as an important food-plant. This tall grass is abundant among the dunes of the gulf shore.

[17] Grinnell, J., *Auk*, **21**, 1904, 364–382.

[18] Dr. C. Wythe Cooke writes to the author: "The northern limit of *Peromyscus polionotus albifrons* as described in your letter of December 12, appears to coincide with the northern boundary of the Citronelle formation [Pliocene], which passes through Vernon, Wausau, and Round Lake. The Citronelle is covered almost everywhere by a mantle of deep, loose, salmon-colored sand, very similar to beach or dune sand, which contrasts sharply with the red or brown loams derived from the Tampa, Glendon and Marianna limestones which lie north of the Citronelle area." My own field notes refer to a transition from predominantly pale sand to predominantly reddish and brown soils, occurring near to, but not at, the boundary of the ranges of *polionotus* and *albifrons*.

[19] Sumner, *J. Mammalogy*, **2**, 1921, 75–86; **7**, 1926, 158.

ON THE LINEAR CONNECTION INDEX OF THE ALGEBRAIC SURFACES $z^n = f(x, y)$

BY OSCAR ZARISKI

DEPARTMENT OF MATHEMATICS, JOHNS HOPKINS UNIVERSITY

Communicated May 11, 1929

1. The purpose of this paper is to prove the following theorem:

THEOREM. *If $n = q^\alpha$ is a power of a prime number and $f(x, y) = 0$ an irreducible algebraic curve, then the linear connection index R_1 of the surface*

$$z^n = f(x,y)$$

is equal to 0.

By this theorem, the above surface is *regular* and does not possess simple integrals of Picard of the 1st and 2nd kind.

The conditon $n = q^\alpha$ is essential, as is shown by an example at the end of the paper.

The theorem has been proved for $n = 2$.[1] In this case De-Franchis[2] has obtained a more expressive result stating that, if the surface $z^2 = f(x, y)$ possesses q simple integrals of the 1st kind ($R_1 = 2q$), then the curve $f(x, y) = 0$ is composed of $2q + 2$ or $2q + 1$ curves belonging to one and the same pencil.

2. We now proceed to the proof of our theorem. We consider the surface F, given by the equation

$$z^n = f(x, y), \tag{1}$$

where, by hypothesis, the curve $f = 0$ is irreducible. Let $C_{\bar{x}}$ be a generic curve of the pencil $| C |$, cut out on the surface F by the planes $x = \text{const.}$, and let p be the genus of $C_{\bar{x}}$. Any one-dimensional circuit Γ on F is homologous (mod. F) to a linear combination of $2p$ independent circuits on $C_{\bar{x}}$.[3] We next proceed to fix a fundamental set of circuits on $C_{\bar{x}}$ in the following manner: Let m be the order of the branch curve f, and let $y_1, y_2, \ldots, y_m$ be the roots of the equation

$$f(\bar{x}, y) = 0.$$

If we consider in the y-plane a set of non-intersecting oriented loops, $g_1, g_2, \ldots, g_m$, surrounding the points $y_1, y_2, \ldots, y_m$, respectively, then, when the variable point y describes the loop g_i, the n branches $z_1, z_2, \ldots, z_n$ ($z_k = \omega^{k-1} z_1$, $\omega = e^{2\pi i/n}$) of the function z are permuted cyclically. To the loop g_i there correspond on $C_{\bar{x}}$ n open overlapping paths starting on different sheets of the n-sheeted Riemann surface of $C_{\bar{x}}$. We still denote

by g_i that path which starts on the first sheet and ends on the second sheet. The remaining $n - 1$ paths may be conveniently denoted by

$$\varphi(g_i),\ \varphi^2(g_i),\ \ldots,\ \varphi^{n-1}(g_i),$$

where the symbol φ^i indicates the transformation

$$z' = \omega^i z,\quad y' = y,\quad x' = x.$$

The circuits on $C_{\bar{x}}$ which we now introduce are the following:

$$\gamma_{i,1} = g_1 - g_{i+1},\ \gamma_{i,2} = \varphi(\gamma_{i,1}) = \varphi(g_1) - \varphi(g_{i+1}),\ \ldots,\ \gamma_{i,n} = \varphi^{n-1}(\gamma_{i,1})$$
$$(i = 1, 2, \ldots, m - 1).$$

The $(m - 1)n$ circuits $\gamma_{i,j}$ are not independent (mod. $C_{\bar{x}}$). In the first place the following $m - 1$ homologies exist:

$$\gamma_{i,1} + \gamma_{i,2} + \ldots + \gamma_{i,n} \sim 0 \text{ (mod. } C_{\bar{x}}). \qquad (2)$$

These are consequences of the homologies:

$$g_i + \varphi(g_i) + \ldots + \varphi^{n-1}(g_i) \sim 0 \text{ (mod. } C_{\bar{x}}).$$

It is immediately seen that if δ denotes the H. C. F. of m and n and if $\delta \neq n$, then the point $y = \infty$ is a branch point of the function z, and that in the neighborhood of $y = \infty$ the branches of z are distributed in δ cycles of order n/δ. From this there follows immediately:

$$2p = (n - 1)(m - 1) - (\delta - 1).$$

Hence, in addition to the homologies (2) there must exist further $\delta - 1$ relations among the circuits $\gamma_{i,j}$. These relations are easily obtained by considering the δ circuits on $C_{\bar{x}}$ which correspond to a circuit in the y-plane surrounding the m points y_i, and by observing that they are all homologous to zero. Apparently we thus obtain δ additional homologies, but it is easily seen that only $\delta - 1$ of these are independent of the homologies (2).

Although the circuits $\gamma_{i,j}$ do not form a minimum fundamental set on $C_{\bar{x}}$, we prefer for reasons of symmetry not to undertake a further reduction.

3. To each generating relation among the generators g_i of the fundamental group G of the curve $f = 0$, there correspond several homologies (mod. F) among the circuits $\gamma_{i,j}$. I proved in a recent paper[4] *that, if the curve f is irreducible, the generators g, are conjugate elements of G.* This is all that we require for our present considerations. We have then

$$g_{i+1} = g^{(i)} g_1 g^{-(i)} \qquad (i = 1, 2, \ldots, m - 1), \qquad (3)$$

where $g^{(i)}$ is a closed path in the y-plane. To $g^{(i)}$ there correspond on

$C_{\bar{x}}n$ (closed or open) overlapping paths starting on different sheets. We still denote by the same symbol $g^{(i)}$ the path which starts on the first sheet, and assume that $g^{(i)}$ ends on the rth sheet. Then $g^{(i)} - \varphi^{r-2}(g_1) - \ldots - \varphi(g_1) - g_1$ is a circuit Γ_i on $C_{\bar{x}}$, i.e.,

$$g^{(i)} = \Gamma_i + g_1 + \varphi(g_1) + \ldots + \varphi^{r-2}(g_1).$$

If $r = 1$, then $g^{(i)}$ is itself a circuit Γ_i.

From the generating relation (3) we deduce the following homology (mod. F):

$$g_{i+1} \sim \Gamma_i + g_1 + \varphi(g_1) + \ldots + \varphi^{r-2}(g_1) + \varphi^{r-1}(g_1) - \varphi^{r-1}(g_1) - \ldots - \varphi^2(g_1) - \varphi(g_1) - \varphi(\Gamma_i),$$

or

$$g_{i+1} \sim \Gamma_i - \varphi(\Gamma_i) + g_1,$$

and finally

$$\gamma_{i,1} + \Gamma_i - \varphi(\Gamma_i) \sim 0. \tag{4}$$

Transforming (4) by $\varphi, \varphi^2, \ldots, \varphi^{n-1}$ we obtain the following system of $n(m-1)$ homologies among the $n(m-1)$ circuits $\gamma_{i,j}$:

$$\gamma_{i,1} + \Gamma_i - \varphi(\Gamma_i) \sim 0, \quad \gamma_{i,2} + \varphi(\Gamma_i) - \varphi^2(\Gamma_i) \sim 0, \ldots, \gamma_{i,n} + \varphi^{n-1}(\Gamma_i) - \Gamma_i \sim 0 \tag{5}$$

$$(i = 1, 2, \ldots, m-1).$$

In (5) the $\Gamma_i's$ are linear combinations of the $\gamma'_{i,j}s$. We prove in the next sections that if n is a power of a prime number, then the determinant Δ of the coefficients of the system (5) is different from zero. Hence, if $n = q^\alpha$, then for any of the circuits $\gamma_{i,j}$:

$$\Delta\gamma_{i,j} \sim 0,$$

and this proves our theorem.

4. Let

$$\Gamma_i \sim \sum_{s=1}^{m-1} \sum_{t=1}^{n} b_{s,t}^{(i)} \gamma_{s,t}.$$

Then, since $\varphi(\gamma_{s,n}) = \gamma_{s,1}$, we have $\varphi(\Gamma_i) \sim \sum_{s=1}^{m-1} \sum_{t=1}^{n} b_{s,t-1}^{(i)} \gamma_{s,t}$, where $b_{s,o}^{(i)}$ must be replaced by $b_{s,n}^{(i)}$. We set

$$a_{s,t}^{(i)} = b_{s,t}^{(i)} - b_{s,t-1}^{(i)} \tag{6}$$

for any value of s and t, except for $s = i$ and $t = 1$, in which case we set

$$a_{i,1}^{(i)} = b_{i,1}^{(i)} - b_{i,n}^{(i)} + 1. \tag{6a}$$

The index i being fixed, the first of the homologies (5) becomes

$$\sum_{s=1}^{m-1} \sum_{t=1}^{n} a_{s,t}^{(i)} \gamma_{s,t} \sim 0. \tag{7}$$

The remaining $n - 1$ homologies can be obtained from (7) by applying successively the substitution

$$(a_{1,1}^{(i)} a_{1,2}^{(i)} \ldots, a_{1,n}^{(i)}) (a_{2,1}^{(i)} a_{2,2}^{(i)}, \ldots, a_{2,n}^{(i)}) \ldots (a_{m-1,1}^{(i)}, a_{m-1,2}^{(i)}, \ldots, a_{m-1,n}^{(i)})$$

to the coefficients.

Hence the matrix of the coefficients $a_{st}^{(i)}$ of the system (5) is made up of $(m-1)^2$ circulants $A_s^{(i)}$ $(s, i = 1, 2, \ldots, m-1)$, where

$$A_s^{(i)} = \begin{Vmatrix} a_{s,1}^{(i)} & a_{s,2}^{(i)} & \ldots & a_{s,n}^{(i)} \\ a_{s,n}^{(i)} & a_{s,1}^{(i)} & \ldots & a_{s,n-1}^{(i)} \\ \cdot & \cdot & \ldots & \cdot \\ a_{s,2}^{(i)} & a_{s,3}^{(i)} & \ldots & a_{s,1}^{(i)} \end{Vmatrix}.$$

We may write our matrix $\| a_{s,t}^{(i)} \|$ symbolically in the following form:

$$A = \| a_{s,t}^{(i)} \| = \begin{Vmatrix} A_1^{(1)} & A_2^{(1)} & \ldots & A_{m-1}^{(1)} \\ A_1^{(2)} & A_2^{(2)} & \ldots & A_{m-1}^{(2)} \\ \cdot & \cdot & \ldots & \cdot \\ A_1^{(m-1)} & A_2^{(m-1)} & \ldots & A_{m-1}^{(m-1)} \end{Vmatrix}.$$

We observe that it follows from (6) and (6a) that

$$\sum_{t=1}^{n} a_{s,t}^{(i)} = \delta_{s,i}, \tag{8}$$

where $\delta_{s,i} = 0$, if $s \neq i$, and $\delta_{ii} = 1$, i.e., the sum of the elements of a row (or of a column) in each matrix $A_s^{(i)}$ is equal to 0, except the main diagonal matrices $A_i^{(i)}$ in which this sum is 1.

In the following section we deduce a formula for the value of the determinant $\Delta = | a_{s,t}^{(i)} |$:

If we put

$$f_s^{(i)}(x) = a_{s,1}^{(i)} + a_{s,2}^{(i)} x + \ldots + a_{s,n}^{(i)} x^{n-1}, \tag{9}$$

and if we form the determinant

$$f(x) = \begin{vmatrix} f_1^{(1)}(x) & f_2^{(1)}(x) & \ldots & f_{m-1}^{(1)}(x) \\ f_1^{(2)}(x) & f_2^{(2)}(x) & \ldots & f_{m-1}^{(2)}(x) \\ \cdot & \cdot & \ldots & \cdot \\ f_1^{(m-1)}(x) & f_2^{(m-1)}(x) & \ldots & f_{m-1}^{(m-1)}(x) \end{vmatrix}, \tag{9a}$$

then

$$\Delta = f(1) f(\omega_1) f(\omega_2) \ldots f(\omega_{n-1}), \tag{10}$$

where $1, \omega_1, \omega_2, \ldots, \omega_{n-1}$ *are all the nth roots of unity.*

The formula (10) extends to determinants made up of circulants the known formula for the evaluation of a circulant.

Using the formula (10) and taking into account the relations (8) we can easily prove that, if $n = q^\alpha$, then $\Delta \neq 0$. In fact, it follows from (8) and (9) that

$$f_s^{(i)}(1) = \delta_{s,i},$$

and hence, from (9a), that

$$f(1) = 1. \tag{11}$$

If, however, $\Delta = 0$, then for some value k, $1 \leq k \leq n-1$, we will have

$$f(\omega_k) = 0. \tag{11a}$$

Let ω_k be a primitive νth root of unity ($n = 0 \pmod{\nu}$), and let

$$\varphi_\nu(x) = 0$$

be the irreducible equation with integer coefficients which ω_k satisfies. By (11a) we have

$$f(x) \equiv 0 \pmod{\varphi_\nu(x)}. \tag{12}$$

It can be easily shown that if $\nu = q^\beta$ is a power of a prime number q, then

$$\varphi_\nu(1) = q. \tag{13}$$

In fact, relation (13) holds for $\beta = 1$, for

$$\varphi_q(x) = x^{q-1} + x^{q-2} + \ldots + x + 1.$$

We prove now that if (13) holds for any β' less than β, then it holds also for β. In fact, we have

$$\varphi_{q^\beta}(x)\varphi_{q^{\beta-1}}(x) \ldots \varphi_q(x) = x^{q^\beta} + x^{q^{\beta-1}} + \ldots + x + 1.$$

Hence,

$$\varphi_{q^\beta}(1) \cdot q^{\beta-1} = q^\beta,$$

and consequently

$$\varphi_{q^\beta}(1) = q. \qquad \text{Q. E. D.}$$

If $n = q^\alpha$, then $\nu = q^\beta$, $\beta \leq \alpha$, and hence from (12) it follows by (13) that

$$f(1) \equiv 0 \pmod{q},$$

which contradicts (11). Thus the hypothesis $\Delta = 0$ leads to a contradiction, and hence

$$\Delta \neq 0.$$

5. To prove the formula (10) we proceed as follows. We consider the matrix

$$d = \left\| \begin{matrix} 1 & 1 & 1 & \dots & 1 \\ 1 & \omega_1 & \omega_2 & \dots & \omega_{n-1} \\ 1 & \omega_1^2 & \omega_2^2 & \dots & \omega_{n-1}^2 \\ . & . & . & \dots & . \\ 1 & \omega_1^{n-1} & \omega_2^{n-1} & \dots & \omega_{n-1}^{n-1} \end{matrix} \right\|$$

and we adopt the following symbolic notation:

$$D = \overbrace{\begin{vmatrix} d & 0 & \dots & 0 \\ 0 & d & \dots & 0 \\ . & . & \dots & . \\ 0 & 0 & \dots & d \end{vmatrix}}^{m-1}$$

for the determinant of order $n(m-1)$, where d stands for the matrix introduced above and each 0 for the zero-matrix of order n. If we now form the product ΔD, it is easily seen that the corresponding determinant can be written symbolically in the form:

$$\Delta D = \begin{vmatrix} d_1^{(1)} & d_2^{(1)} & \dots & d_{m-1}^{(1)} \\ d_1^{(2)} & d_2^{(2)} & \dots & d_{m-1}^{(2)} \\ . & . & \dots & . \\ d_1^{(m-1)} & d_2^{(m-1)} & \dots & d_{m-1}^{(m-1)} \end{vmatrix}, \tag{14}$$

where each element $d_s^{(i)}$ stands for the following matrix:

$$d_s^{(i)} = \left\| \begin{matrix} f_s^{(i)}(1) & f_s^{(i)}(\omega_1) & \dots & f_s^{(i)}(\omega_{n-1}) \\ f_s^{(i)}(1) & \omega_1 f_s^{(i)}(\omega_1) & \dots & \omega_{n-1} f_s^{(i)}(\omega_{n-1}) \\ . & . & \dots & . \\ f_s^{(i)}(1) & \omega_1^{n-1} f_s^{(i)}(\omega_1) & \dots & \omega_{n-1}^{n-1} f_s^{(i)}(\omega_{n-1}) \end{matrix} \right\|.$$

Let us now consider the Laplace expansion of the determinant (14) in terms of the elements of the columns of order $1 + k$, $1 + k + n$, $1 + k + 2n$, . . ., $1 + k + (m-2)n$ $(0 \leq k \leq n-1)$. We denote by B_k the matrix composed of these columns. Any determinant of order $m-1$ extracted from the matrix B_k has the following form:

$$\begin{vmatrix} \omega_k^{j_1} f_1^{(i_1)}(\omega_k) & \omega_k^{j_1} f_2^{(i_1)}(\omega_k) & \dots & \omega_k^{j_1} f_{m-1}^{(i_1)}(\omega_k) \\ \omega_k^{j_2} f_1^{(i_2)}(\omega_k) & \omega_k^{j_2} f_2^{(i_2)}(\omega_k) & \dots & \omega_k^{j_2} f_{m-1}^{(i_2)}(\omega_k) \\ . & . & \dots & . \\ \omega_k^{j_{m-1}} f_1^{(i_{m-1})}(\omega_k) & \omega_k^{j_{m-1}} f_2^{(i_{m-1})}(\omega_k) & \dots & \omega_k^{j_{m-1}} f_{m-1}^{(i_{m-1})}(\omega_k) \end{vmatrix}, \tag{15}$$

where $i_1, i_2, \dots, i_{m-1}$ are numbers of the series $1, 2, \dots, m-1$, $i_1 \leq i_2$

$\leq \ldots \leq i_{m-1}$, and $j_1, j_2, \ldots, j_{m-1}$ are numbers of the series $0, 1, 2, \ldots, n-1$. Every determinant (15), in which two of the indices i are equal, vanishes. Hence in the non-vanishing determinants we must have $i_1 = 1, i_2 = 2, \ldots, i_{m-1} = m-1$, and so, by (9a), the value of such a determinant is equal to

$$f(\omega_k) \cdot \omega_k^{j_1 + j_2 + \cdots + j_{m-1}}.$$

Thus all non-vanishing determinants (15) have a common factor $f(\omega_k)$. If we then consider the matrix C_k of as many rows and columns as B_k ($(m-1)\,n$ rows, $m-1$ columns):

$$C_k = \left\| \begin{array}{cccc} 1 & 0 & \ldots & 0 \\ \omega_k & 0 & \ldots & 0 \\ \cdot & \cdot & \ldots & \cdot \\ \omega_k^{n-1} & 0 & \ldots & 0 \\ 0 & 1 & \ldots & 0 \\ 0 & \omega_k & \ldots & 0 \\ \cdot & \cdot & \ldots & \cdot \\ 0 & \omega_k^{n-1} & \ldots & 0 \\ \cdot & \cdot & \ldots & \cdot \\ \cdot & \cdot & \ldots & \cdot \\ 0 & 0 & \ldots & 1 \\ 0 & 0 & \ldots & \omega_k \\ \cdot & \cdot & \ldots & \cdot \\ 0 & 0 & \ldots & \omega_k^{n-1} \end{array} \right\|,$$

We see by mere inspection that every determinant (15) extracted from the matrix B_k is equal to the corresponding determinant extracted from the matrix C_k multiplied by the factor $f(\omega_k)$. Consequently the value of the determinant (14) remains unaltered if we replace in it the elements of the columns of order $k+1, k+1+n, \ldots, k+1+(m-2)n$ by the elements of the columns of the matrix C_k, provided we multiply the resulting determinant by the factor $f(\omega_k)$. If this is done successively for $k = 0, 1, \ldots, n-1$, the determinant (14) is reduced to the following form:

$$\Delta D = f(1)\, f(\omega_1)\, f(\omega_2) \ldots f(\omega_{n-1}).\quad D',$$

where the new determinant D' is easily seen to be nothing else than the determinant D. Hence $D' = D$, and consequently

$$\Delta = f(1)\, f(\omega_1)\, f(\omega_2) \ldots f(\omega_{n-1}),$$

which proves the formula (10).

6. We want to show in this section by an actual example that the con-

dition $n = q^{\alpha}$, under which we proved our theorem, is essential. Let us consider the surface F given by the following equation:

$$z^6 = \varphi^2(x, y) + \psi^3(x, y), \tag{16}$$

where $\varphi = 0$ and $\psi = 0$ represent a cubic curve and a conic, respectively. Here the branch curve of the function z is an irreducible sextic. However, we show that F possesses a simple integral of Picard of the 1st kind. In fact, if we consider the following pencil of surfaces:

$$\psi(x, y) - t z^2 = 0, \tag{17}$$

where t is a parameter, by eliminating ψ between (16) and (17) we have the equation

$$z^6(1 - t^3) - \varphi^2(x, y) = 0. \tag{18}$$

But the surface (18) breaks up into two surfaces

$$\varphi + z^3\sqrt{1 - t^3} = 0,$$

$$\varphi - z^3\sqrt{1 - t^3} = 0.$$

and this shows that the generic curve C of the pencil $| C |$ cut out on F by the surfaces of the pencil (17) breaks up into two curves $D = D_1$, $D = D_2$. When C varies in the *linear* pencil $| C |$, the curve D varies in an *elliptic* pencil $| D |$. In fact, the elements of the pencil $| D |$ are in one-to-one correspondence with the points of the elliptic curve

$$u^2 = 1 - t^3. \tag{19}$$

The abelian integral of the 1st kind

$$u = \int \frac{dt}{u},$$

attached to the curve (19), evidently becomes a simple integral of Picard of the 1st kind attached to the surface F, when we put

$$t = \frac{\psi}{z^2}, \; u = \frac{\varphi}{z^3}.$$

Hence the surface (16) is irregular, $R_1 > 0$, and—we observe incidentally—it can be easily shown that $R_1 = 2q = 2$.

[1] H. Lacaze, "Sur la connexion linéaire de quelques surfaces algébriques," *Ann. Faculté Sciences l'Université Toulouse*, 2nd series, **3**, 1901, pp. 151–215.

[2] De-Franchis, "I piani doppi dotati di due o più differenziali totali di prima specie," *Rendiconti dell' Accademia Lincei*, 5th series, **13**, pp. 688–695 (1904).

[3] See E. Picard and G. Simart, *Théorie des fonctions algébriques de deux variables indépendantes*, **1**, Chapt. IV, sec. 11, p. 86 (Paris, Gauthier-Villars, 1897); S. Lefschetz, *L'Analysis Situs et la géometrie algébrique*, p. 33 (Paris, Gauthiers-Villars, 1924).

[4] "On the problem of existence of algebraic functions of two variables possessing a given branch curve," *Am. J. Math.*, **51**, No. 2, April, 1929.

THE OCCURRENCE OF A NICOTIANA GLUTINOSA HAPLONT

By Thomas Harper Goodspeed and Priscilla Avery

Department of Botany, University of California

Communicated April 22, 1929

In recent reports[1,2] of the discovery of haploid Angiosperms attention has been directed to the relative frequency with which they occur in various genera of the Solanaceae. The present note adds another species of this family to the rapidly increasing list of angiospermous haplonts, the first of which were described in 1922 by Blakeslee[3] and his co-workers. Seven haploid plants of *N. Tabacum* have occurred in our cultures in F_1 interspecific progenies.[4] All previous haplonts have been found either in F_1 of interspecific hybrids or in progenies artificially subjected to abnormal environmental influences or in cultures characterized by a segregating factorial composition or an unbalanced chromosomal condition. The single haploid individual of *N. glutinosa* found in the summer of 1928 is apparently the first instance in which such a plant has occurred in a pure-line progeny.

The species *glutinosa* is included in the *Rustica* section of the genus although it might be better placed in *Tabacum* especially if *tomentosa*, with which it has certain affinities, is included in the latter section.[5] It is a strictly monotypic species of some horticultural interest and is widely grown in botanical gardens. Although quite distinct in external morphology from almost all other *Nicotiana* species, F_1 hybrids have been produced with a number of them belonging to all three sections of the genus. It possesses 12 pairs of chromosomes. It is interesting to note that Levine[6] has found $4n$ cells in induced neoplasmic tissue in this species.

The *glutinosa* haplont was one of 24 plants which grew from seedlings which were subjected to x-radiation 5 weeks after germination. The seedlings at the time of treatment had produced from 5–7 small, true leaves which for some weeks thereafter gave evidence of considerable abnormality in growth and development. The effect on external morphology was in most cases ephermeral and when put out into the field all the young plants except two were normal in appearance. These two were so slow growing and poorly developed that they were held for some weeks in the green house. One of them, the haplont, became more vigorous and was ultimately set out in the field; the other remained small and weak and after some months came to flower and set selfed seed on a single shoot less than 6 inches long. Undoubtedly the occurrence of the haplont was spontaneous and in no wise to be referred to the treatment received during the seedling stages.

The haploid plant was, in a general way, a replica of its diploid parent

on a considerably reduced scale. The flower color was a greenish yellow rather than a salmon-red and flower and leaf form were considerably altered. Its anthers were small and shriveled and no selfed seed was set, nor did its eggs or pollen grains set seed with gametes of diploid plants after the relatively few pollinations which were made. The plant continued to send up basal shoots and to grow vigorously long after the diploid plants had ceased to flower.

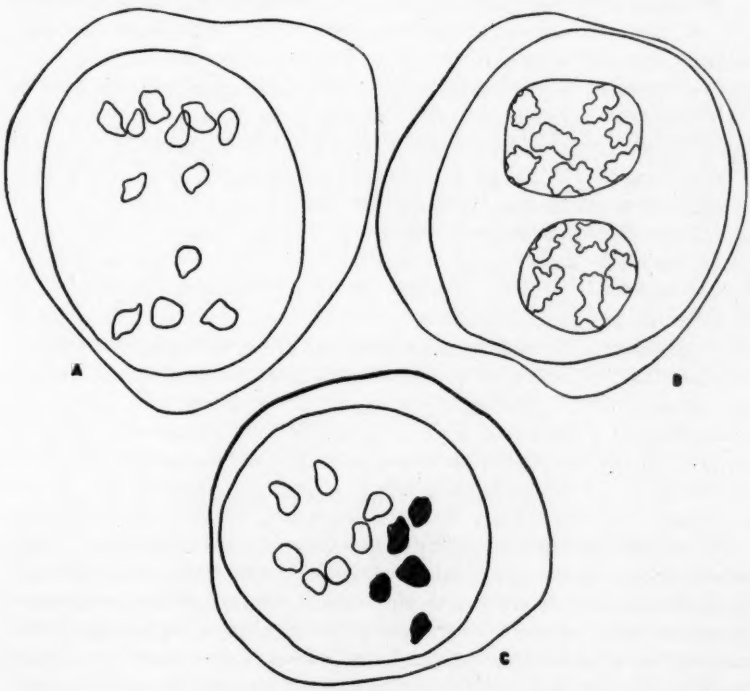


FIGURE 1

Nicotiana glutinosa (n = 12)—haplont. P.M.C. *a*, I-A, lateral view, 4–8 chromosome distribution still under way; *c*, later I-A, polar view, 5–7 distribution completed; *b*, interkinesis, a 5–7 distribution. Aceto-carmine preparations.

In somatic tissues the chromosome number of this plant was 12 and at *I-M* 12 univalents were found. The appearance of *I-A* and interkineses in P. M. C. is illustrated in figure 1. There was apparently no true conjugation within the chromosome group and the 12 large units were exceedingly well distributed and easy to count at *I-A*. This statement applies to E. M. C. as well as P. M. C. Random distribution of the 12 univalents was the rule and no cytoplasmic or other disturbances such as

were seen in *Tabacum* and *Triticum* haplonts were observed. Suspended *I-A* stages followed by equational division were not infrequent and were reflected in the occurrence of dyads at the tetrad stage. Otherwise, division of univalents at *I-A* rarely, if ever, took place according to *II-M* counts, which uniformly gave a total of 12 units in the two plates. *II-M* counts also showed that all types of distribution, on the basis of random assortment at *I-A*, occurred—6–6, 7–5, 8–4, 9–3, 10–2, 11–1 and all 12 in a single *II-M* plate having been observed. Further cytological studies of the *glutinosa* haplont are in progress and will be reported on at a later date.

[1] Lindstrom, E. W., *J. Hered.*, **20**, 23–30, 1929.
[2] Hollingstead, L., *Amer. Nat.*, **62**, 1928.
[3] Blakeslee, A. F., Belling, J., Farnham, M. E., and Bergner, D., *Science*, N. S., **55**, 646–7, 1922.
[4] Ruttle, M. L., *Univ. Calif. Publ. Bot.*, **11**, 12, 233–244, 1928.
[5] East, E. M., *Biblio. Genetica*, **4**, 244–320, 1928.
[6] Levine, M., *Phytopath.*, **19**, 97, 1929.

FURTHER REMARKS CONCERNING THERMIONIC "A" AND "b," A REVISION AND EXTENSION

BY EDWIN H. HALL

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

Read before the Academy, April 23, 1929

This paper is written in continued support of the thesis that all the known facts regarding thermionic emission from metals are consistent with the original conception of Richardson, which assumed the emitted electrons to come from a body of free electrons sharing the energy of thermal agitation within the metal. In the course of the paper I shall have occasion to revise some remarks which I have made concerning the equality of "A" in different metals, and I shall consider the possibility that the photo-electric work function, represented by "b_0," is variable with temperature, but nothing that I have to say involves any departure from the fundamental conceptions of the dual theory of electric conduction which I so many times set forth in print.

There is a strong tendency at present to identify the thermionic work function and the photo-electric work-function, numerically at least. This tendency is represented on the experimental side by DuBridge[1] and Warner[2], and on the theoretical (thermodynamical) side by Bridgman.[3] In the abstract of a recent paper[4] Bridgman says, "The thermionic work-function and the photo-electric work function are found to

differ by a universal constant, which must be zero in the light of the work of Warner and the recent work of DuBridge."

All of this may seem highly unfavorable to my thesis that electric conduction in metals is carried on by electrons in two different states, the "free" electrons, or "thermions," which are the ones issuing in thermionic emission, and the "associated," or "valence," electrons, which are the ones expelled in photo-electric action. I shall, however, undertake to show that all the evidence referred to, both experimental and thermodynamical, is entirely consistent with the thesis just stated above.

I shall deal with Bridgman's argument first, and show that his definition of work-function is something essentially different from that which holds in actual experiments upon emission. Let ϕ represent, in ergs, the thermionic work function, which I shall define as the amount of work which must be done against opposing forces in the escape of one electron thermionically from the metal. Let ϕ_0 represent, in ergs, the photo-electric work function, which I shall define as the amount of energy which must be supplied in order to take an electron photo-electrically from the metal. I assume, in accordance with Richardson's original "classical kinetic theory," that in thermionic emission the thermal energy of the electron is the same after emission as before—namely, that of a monatomic gas molecule corresponding to the temperature of the metal and the surrounding space. For simplicity in the present argument I shall suppose that the photo-electrically emitted electrons are left in exactly the same state of energy as those emitted thermionically, and, as my ϕ_0 does not provide for the thermal energy of the electron after emission, I must make an additional contribution of energy, θ let us call it, on this account. I assume, keeping thus to the view which, I think, has prevailed till recently, that thermionic emission uses electrons which have been already loosed from atoms within the metal, leaving an equal number of positive ions, while photo-electric emission takes electrons which are parts of atoms. I shall represent by λ' the amount of energy required to ionize an atom within the metal—that is, to change an atom into an ion and a "free" electron within the metal, this electron having after the operation the full quota of thermal energy corresponding to the temperature of the metal.

With the definitions given above we must by the first law of thermodynamics have

$$\lambda' + \phi = \phi_0 + \theta, \quad \text{or} \quad \phi = \phi_0 - (\lambda' - \theta). \tag{1}$$

Now let us take Bridgman's point of view. He considers emission from an electrically isolated piece of metal, and by work function he means not only the energy required for the act of emission but in addition what may be called the *heat of adjustment*, whatever supply of energy, positive

or negative, may be required to restore a state of equilibrium within the metal after its loss of electrons.

Let us suppose, for example, that ν electrons have been expelled by thermionic action from the isolated metal. The heat energy called for in the emission operation proper is $\nu\phi$, but, if no adjustment were to occur within the metal, it would have ν less free electrons than at first, with an unchanged number of positive ions. Such a condition cannot last. The mass law of equilibrium requires that $^1/_2\nu$ atoms shall become ionized, so that in the final state there shall be $^1/_2\nu$ less free electrons and $^1/_2\nu$ more positive ions than there were in the metal at first. The amount of energy demanded for this ionization is $^1/_2\ \nu\lambda'$, so that the total amount of energy which has been called for is

$$\nu\phi + {}^1/_2\nu\lambda',$$

which is Bridgman's thermionic work function multiplied by ν.

Let us now suppose that the ν electrons had been expelled by photo-electric action. The energy requirement for the emission and thermal elevation of these electrons would be $\nu(\phi_0 + \theta)$, but the operation would, without adjustment, leave the metal containing ν more positive ions than at first, with no change in the number of free electrons. The mass law would come into operation, requiring $^1/_2\nu$ free electrons to unite with an equal number of ions, so that the final condition would be precisely that which followed thermionic emission, $^1/_2\nu$ fewer free electrons and $^1/_2\nu$ more ions than at the start. The union of the free electrons with the ions would *yield* $^1/_2\nu\lambda'$ in heat energy, and so we should have

$$\nu(\phi_0 + \theta) - {}^1/_2\nu\lambda'$$

as Bridgman's photo-electric work function multiplied by ν. Evidently, since the initial and also the final state is the same in this case as in the preceding one, we must have

$$\nu\phi + {}^1/_2\nu\lambda' = \nu(\phi_0 + \theta) - {}^1/_2\nu\lambda', \qquad (2)$$

or

$$\phi = \phi_0 - (\lambda' - \theta),$$

which is precisely my eq. (1).

Of course, the positive charge which results from the emission of electrons appears finally at the surface of the metal, the interior parts having at the end as at the beginning as many free electrons as positive ions per unit volume. In discussing the "heat of adjustment" we have been concerned with the so-called "surface heat" of charging.

Let us consider now the experimental evidence which may be supposed to show the numerical identity of the thermionic and the photo-electric work functions, the ϕ and ϕ_0 which have been defined above. I shall

deal with this matter at considerable length, in the hope of clearing up the mystification, or confusion of ideas, which seems to exist regarding the formulas of thermionic emission. If any readers are inclined to think that the modification of Richardson's equations by the introduction of my own peculiar notions must add to the confusion, I beg them to read my argument through before they reject it.

Starting with the conceptions of Richardson's "classical kinetic theory," as set forth on pages 33 and 34 of his *Emission of Electricity from Hot Bodies*, I shall let n equal the number of free electrons per cu. cm. within the metal, and n' the number of electrons per cu. cm. outside the metal, equilibrium conditions being assumed. Then, if ϕ has the meaning already given it in this paper and if $b = \phi \div k$, we have, according to the Boltzmann distribution law,

$$n' = n\epsilon^{-\frac{\phi}{kT}} = n\epsilon^{-\frac{b}{T}}. \tag{3}$$

In a previous paper[5] I have, following Richardson's reasoning, shown that the thermionic emission current from one sq. cm. of the metal surface is

$$I = Fe.n'.T^{0.5}, \tag{4}$$

F being a constant, 1.56×10^5, given, like the factor $T^{0.5}$, by the kinetic theory of gases, while e is the electron charge. Making use of eq. (3) we get from (4)

$$I = Fe.n.T^{0.5}.\epsilon^{-\frac{b}{T}}. \tag{5}$$

Now Richardson, near the top of page 34, assumes that

$$n = zT^{1.5}, \tag{6}$$

z being a constant. With this assumption we get from (5)

$$I = Fe.zT^{1.5}.T^{0.5}.\epsilon^{-\frac{b}{T}}, \tag{7}$$

or, if we put A for $Fe.z$, which is a constant,

$$I = AT^{1.5}.T^{0.5}.\epsilon^{-\frac{b}{T}} = AT^{2}\epsilon^{-\frac{b}{T}}, \tag{8}$$

which is one of the two familiar Richardson expressions for the emission current.

If, on the other hand, we assume that n is a constant independent of temperature and write $A = Fe.n$, we get from (5)

$$I = AT^{0.5}\epsilon^{-\frac{b}{T}}, \tag{9}$$

which is the other familiar Richardson equation.

I think this simple explanation of the relation between these two for-

mulas, (8) and (9), is not generally perceived. Of course, both equations cannot be right for the same metal, and, if experiment fails to decide which is the better, it may very well be that neither is the best possible expression of fact. I shall return to this idea farther on. Present custom inclines, I think, to use (8) rather than (9), and this may perhaps be interpreted as a tendency, not generally recognized as such, toward the acceptance of eq. (6). I shall make no further use in this paper of eq. (9).

Now as to the b in eq. (8), is it or is it not a constant, according to experimental evidence? This is a question which must not be answered hastily. Undoubtedly experimental evidence is in good agreement with a formula of the same type as eq. (8) having the A constant and having some constant where b is in (8). But does this constant which corresponds in place with b necessarily have the same meaning, the same definition, as that which is given above for b? No.

Thus, let us suppose that b, as defined, is a function of temperature

$$b = b_0 - aT, \tag{10}$$

where b_0 and a are constants. From eq. (8) by means of (10) we get

$$I = AT^2 \exp\left[-\frac{b_0 - aT}{T}\right] = A\epsilon^a T^2 \epsilon^{-\frac{b_0}{T}}. \tag{11}$$

Writing A_0 for $A\epsilon^a$ we get

$$I = A_0 T^2 \epsilon^{-\frac{b_0}{T}}. \tag{12}$$

It is, I think, this eq. (12), rather than eq. (8), which has been tested so often by means of thermionic emission data and has been found to hold fairly well. Of course, if it can be shown that the a of eq. (10) is zero, eqs. (8) and (12) are identical, A_0 being the same as A and b_0 the same as b, but proof that a is zero is entirely wanting.

In making this statement I am repeating, with some change of form, an argument which I published[6] only a few months ago. I am now going over the matter again because I find that my previous discussion of it was misunderstood at first by at least one specialist in electronic emission, who thought I was merely repeating Bridgman's suggestion of a temperature variation in the *photo-electric* work function. What I am insisting upon is the possibility of a temperature variation of the thermionic work function even in cases where the photo-electric work function is independent of temperature. The difficulty I meet in trying to make my meaning clear is striking proof of the firmness with which the conception of identity between the two work functions is already established in the minds of some investigators in this field. I shall discuss later in this

paper the possible variation of the photo-electric work function with temperature.

This belief in the equality of the two work functions is based largely on the fact that the value of b_0 in the experimentally approved eq. (12) is found to be, within the limits of experimental error, in accord with the experimentally found value of the photo-electric work function. That is $b_0 = \phi_0 \div k$. Now the reader may well ask at this point whether my assumption that the b of eq. (8) is a different quantity from b_0, as indicated by eq. (10), is anything more than the recognition of an academic possibility. Is there, then, any cogent argument tending to show that the a in eq. (10) is not zero?

I was led years ago by my study of thermo-electric effects and conduction data, with no reference to the phenomena of emission, to adopt as approximately true for moderate temperatures, between 0°C. and 100°C., this formula,

$$\lambda' = \lambda'_\epsilon + skT, \tag{13}$$

in which λ' represents, in ergs, the amount of energy needed to take an electron from an atom and leave it "free," with its full complement of thermal energy, within a metal. In this equation λ'_ϵ and s were taken, provisionally, as constants for any given metal, and λ'_ϵ was small compared with skT even between 0° and 100°C. This formula served me pretty well in dealing with the phenomena I was studying when I adopted it, and I found definite values, doubtless more or less inaccurate, for λ'_ϵ and s in the case of many metals, values which I published[7] eight years ago. When, later, I began to give serious attention to the phenomena of electron emission, it occurred to me to try the experiment of supposing this equation to hold, approximately, at the high temperatures of measurable emission. At such temperatures λ'_ϵ would be negligible compared with skT, and so it would practically disappear from the equation.

This being understood, if we write ckT for the θ of eq. (1), this equation (1) becomes,

$$\phi = \phi_0 - (s - c)kT, \tag{14}$$

and dividing by k we get, according to definitions already given,

$$b = b_0 - (s - c)T = b_0 - aT, \tag{14'}$$

which is eq. (10).

I wish especially to emphasize the fact that eq. (13), together with another equation, (15), presently to be given, has proved useful in the explanation of thermo-electric phenomena, for this is no inconsiderable argument in its favor. Thermo-electric effects are small but they are uncompromisingly real and big enough to wreck any electron theory of metals that is framed in disregard of them.

The second equation referred to in the preceding paragraph is

$$n = zT^q, \tag{15}$$

which closely resembles eq. (6), the only difference being the substitution of q in place of 1.5 as the exponent of T. In the studies to which I have already alluded I was led to adopt this eq. (15), with values of q varying from 1.2 in bismuth and in iron to 1.6 in nickel, palladium, and platinum, the mean of all the values being 1.47, a number strikingly close to the value 1.5 assumed by Richardson as holding for metals in general. If now, seeking to revise Richardson's emission formula in accordance with my own notions of electric conduction, I return to eq. (5), I get from it by use of eqs. (10) and (15)

$$I = Fe.\epsilon^a.zT^q.T^{0.5}.\epsilon^{-\frac{b_0}{T}}. \tag{16}$$

Then, putting A' for the approximately constant quantity $Fe\epsilon^a z$, I have

$$I = A'T^q.T^{0.5}\epsilon^{-\frac{b_0}{T}}. \tag{17}$$

Here again I am reproducing, with some changes of form, matter that I have already published.[8] I have shown (see eq. (23) of the paper just referred to) that according to my theory the factor $\epsilon^a z T^q$ of (16), and so the factor $A'T^q$ of (17), should be the same for all metals. But, as q is different for different metals, A' cannot be the same for all metals.

My conclusion that the factor $\epsilon^a z T^q$ should in general be the same for different metals follows from my conception of the Volta effect between metals, and it can be reached, though it was not so reached in my previous discussion of the matter, without any reference to the phenomena of electron emission. Perhaps the argument is worth giving here. In a paper called *Conditions of Electric Equilibrium at Boundary Surfaces*[9] are given the two equations

$$e(P + P_a)_\alpha + \kappa_\alpha = e(P + P_a)_\beta + \kappa_\beta \tag{18}$$

and

$$\frac{n_\alpha}{n_\beta} = \exp\left[-e\frac{(P + P_f)_\alpha - (P + P_f)_\beta}{kT}\right]. \tag{19}$$

In these equations subscript α indicates one metal and subscript β another metal, the two metals being supposed in contact with each other; n_α is the number of free electrons per unit volume in α, n_β the number in unit volume of β. For the meaning of the other terms and for the derivation of the two equations here reproduced I will refer the reader to the paper cited.

I rewrite (18) in the form

$$e(P_\alpha - P_\beta) = (eP_a + \kappa)_\beta - (eP_a + \kappa)_\alpha. \tag{20}$$

Substituting for $e(P_\alpha - P_\beta)$ in (19) the value given by (20), I get

$$\frac{n_\alpha}{n_\beta} = \exp\left[-\frac{(e(P_f - P_a) - \kappa)_\alpha - (e(P_f - P_a) - \kappa)_\beta}{kT}\right]. \quad (21)$$

Now the definition of the various terms here involved is such that, λ' being defined by (13),

$$(eP_a + \kappa + \lambda')_\alpha = e(P_f)_\alpha + 2.5\,kT,$$

whence

$$(e(P_f - P_a) - \kappa)_\alpha = \lambda'_\alpha - 2.5\,kT, \quad (22)$$

where $2.5\,kT$ is the total thermal energy acquired by an electron when it is "freed" within the metal. A like equation holds for β.

Accordingly, (21) reduces to

$$\frac{n_\alpha}{n_\beta} = \exp\left[\frac{\lambda'_\beta - \lambda'_\alpha}{kT}\right]. \quad (23)$$

But, as λ' at high temperatures becomes practically skT, we get for such temperatures

$$(n\epsilon^s)_\alpha = (n\epsilon^s)_\beta, \quad (24)$$

and so, by use of equation (15),

$$(\epsilon^s z T^q)_\alpha = (\epsilon^s z T^q)_\beta, \quad (25)$$

or, since $a = s$ minus c, a universal constant (see eqs. (14) and (14[1])),

$$(\epsilon^a z T^q)_\alpha = (\epsilon^a z T^q)_\beta. \quad (26)$$

Of course, if $\epsilon^a z T^q$ is the same for all metals at the same temperature, $Fe\epsilon^a z T^{(q+0.5)}$ of eq. (16), or the $A'T^{(q+0.5)}$ of eq. (17), is the same for all metals at the same temperature. If now we choose to give the quantity A_0 such a meaning that always

$$A_0 T^2 = A' T^{(q+0.5)}, \quad (27)$$

A_0 must be the same for all metals. But by use of (27) we reduce (17) to the exact form of (12), the familiar Richardson equation. So we must conclude that the A_0 in (12) is a universal constant. Of course, if q is not 1.5, A' and A_0 cannot both be strictly independent of temperature. My s of eq. (13), and so my ϵ^a factor in the value of A_0 and A', may vary somewhat with temperature; so, too, may my q of eq. (15). A_0, as a "universal constant," may seem more imposing than my A', but its advantage in dignity is gained by a loss of physical definiteness. It has an artificial, though exalted, status.

On the other hand, the A of eq. (8) cannot be the same for different metals, unless the a of eq. (10) is the same for all metals.

Thus far I have ignored the possibility that the photo-electric work-function, ϕ_0, and so $\phi_0 \div k$, which is the b_0 of eqs. (12) and (17), may be a function of T. But Du Bridge[10] has found by experiment a temperature change in the photo-electric work-function of platinum, and Bridgman, in a paper[11] already referred to, has discussed the consequences of such a variation. I have nothing to add regarding this matter to what these investigators have discovered, but I will comment briefly upon it in order to bring out clearly the relation of this variation to that variation of the thermionic work-function which I have indicated in eq. (10).

Let us suppose that the following relation holds:

$$\phi_0 = \phi_0' - \gamma kT, \tag{28}$$

ϕ_0' and γ being constants. Then we should have also, after dividing by k,

$$b_0 = b_0' - \gamma T. \tag{29}$$

Using this value of b_0, we get from eq. (12)

$$I = A_0 \epsilon^{\gamma} T^2 \epsilon^{-\frac{b_0'}{T}}, \tag{30}$$

and from (17)

$$I = A' \epsilon^{\gamma} T^{(q+0.5)} \epsilon^{-\frac{b_0'}{T}}. \tag{31}$$

Now I have been able to show, by use of eq. (26), that the A_0 of eq. (12) is, after absorbing the factor ϵ^a which results from eq. (10), a "universal constant." But I have no equation, corresponding to (26), for showing that $A'\epsilon^{\gamma}T^q$, of eq. (31), should be the same for all metals, and so I have no way of proving that $A_0\epsilon^{\gamma}$ of eq. (30), is a universal constant. If we choose to put A_0' for $A_0\epsilon^{\gamma}$, we get from (30)

$$I = A_0' T^2 \epsilon^{-\frac{b_0'}{T}}. \tag{32}$$

This eq. (32) is of precisely the same type as eq. (12), if the b_0 of (12), like the b_0' of (32), is a constant. But metals which in their emission behavior conform to eq. (32) may have an A_0' value which, because of the absorbed factor ϵ^{γ}, will be very different from the "universal constant" value of A_0.

To put the matter in another way, the question whether a in eq. (10) has a value differing from zero cannot be tested by means of emission data, because the presence of a factor ϵ^a in the A_0 of eq. (12) will not cause the value of A_0 to depart from the "universal constant" standard. But the question whether γ in eq. (29) is different from zero can be tested by

emission data, for the factor ϵ^{γ} in the A_0' of eq. (32) will, if γ is not 0, cause A_0' to have an "abnormal" value different from the "universal constant."

Accordingly I cannot by means of electron-emission data test the truth of my proposition that ϕ and ϕ_0 are numerically different, a proposition of great importance in my theory of dual conduction. I can merely show, as I believe the arguments of this paper, taken with those I have previously made,[12] have shown, that no facts already known to us through the study of emission presents any obstacle to the acceptance of this proposition. The evidence in favor of it, and so in favor of my dual conduction theory, is to be sought elsewhere, particularly in the phenomena of thermo-electric action and in the Volta potential-difference. I believe that no uniformitarian theory of conduction in metals has dealt successfully with these effects.

Summary.—If ϕ is the thermionic work-function, defined as the amount of work against opposing forces required to remove an electron from a metal by thermionic action, and if ϕ_0 is the photo-electric work-function, defined as the amount of energy which must be supplied in order to take an electron photo-electrically from the same metal, both experimental evidence and thermodynamic argument are in accord with the proposition that

$$\phi = \phi_0 - akT, \qquad (A)$$

where a is a number, approximately constant, characteristic of the metal, and k is the gas constant for a single molecule. If we let $b_0 = \phi_0 \div k$, and $b = \phi \div k$, eq. (A) becomes

$$b = b_0 - aT. \qquad (B)$$

Proof that (B) is in accord with experimental evidence, as furnished by emission data, has been given in a previous paper (see footnote 6); the thermodynamic argument is given for the first time in the present paper. It is there shown that, when Bridgman gives a thermodynamic proof that the photo-electric work-function and the thermionic work-function must be equal or must differ only by a universal constant, he is using a definition of work-function essentially different from that employed in the definitions given above for ϕ_0 and ϕ.

1. *If ϕ_0, and so b_0, is a constant independent of T:* In this case the author's ideas, applied in accordance with the general "classical kinetic theory" of thermionic emission originally framed, though later discarded, by Richardson, give as the expression for thermionic emission

$$I = Fe \cdot \epsilon^{a} \cdot zT^{q} \cdot T^{0.5} \epsilon^{-\frac{b_0}{T}}, \qquad (C)$$

where Fe is a universal constant and zT^q, z and q being approximately

constants, represents n, the number of "free" electrons in unit volume of the metal. Putting A' for $Fe \cdot \epsilon^a z$, we get from (C)

$$I = A' T^q \cdot T^{0.5} \cdot \epsilon^{-\frac{b_0}{T}}. \qquad (D)$$

It is shown that $A'T^q$ is the same for all metals at the same temperature, but, as q is different for different metals, though in most cases not far from 1.5, A' is not the same for all metals and is not, in general, strictly a constant for any given metal.

If we choose to give A_0 such a value that $A_0 T^{1.5}$ shall be always equal to $A'T^q$, then A_0 must be a universal constant, and with this substitution eq. (D) becomes

$$I = A_0 T^2 \cdot \epsilon^{-\frac{b_0}{T}}, \qquad (E)$$

the familiar Richardson form.

2. *If the photo-electric work-function is a function of temperature, to be represented now by* $\phi_0 - \gamma kT$, *where* ϕ_0 *and* γ *are constants:* In this case we must put $b_0 - \gamma T$ in place of b_0, and thus we get, in place of eq. (D),

$$I = \epsilon^{\gamma} \cdot A' T^q \cdot T^{0.5} \cdot \epsilon^{-\frac{b_0}{T}}. \qquad (F)$$

and in place of (E)

$$I = \epsilon^{\gamma} A_0 T^2 \epsilon^{-\frac{b_0}{T}}.$$

The factor ϵ^{γ} corresponds exactly to the factor ϵ^{α} which Du Bridge, following a suggestion of Bridgman, has used in a recent paper. Du Bridge[13] has nothing corresponding to the factor ϵ^a of eq. (C), or, rather, he treats this factor as 1 in all cases, assuming a, in eq. (B), to be zero.

[1] *Phys. Rev.*, **31**, 236, 1928.
[2] *Proc. Nat. Acad. Sci.*, **13**, 56, 1927.
[3] *Phys. Rev.*, **31**, 90, 1928.
[4] *Ibid.*, **31**, 862, 1928.
[5] *Proc. Nat. Acad. Sci.*, **13**, 315–326, 1927.
[6] *Ibid.*, **15**, pp. 126–127, 1929.
[7] *Ibid.*, **7**, 98–107, 1921.
[8] *Ibid.*, **13**, 315–326, 1927.
[9] *Ibid.*, **11**, 111–116, 1925.
[10] *Ibid.*, **14**, 792, 1928.
[11] *Phys. Rev.*, **31**, 862, 1928.
[12] See, for example, my discussion of "pulled out" electrons in *Proc. Nat. Acad. Sci.*, **15**, 241–251, 1929.
[13] I think that Du Bridge, after a recent correspondence between us, makes no objection to the views which I have expressed in this paper, though he doubtless reserves judgment as to some of them.

ON THE RAMAN EFFECT IN DIATOMIC GASES. II

BY F. RASETTI

NORMAN BRIDGE LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated May 13, 1929

In a recent paper[1] the writer has pointed out how the phenomena observed in the incoherent scattering of light by molecules can be easily accounted for with the quantum theory of dispersion. Kemble and Hill,[2] Langer[3] and Dieke[4] have independently developed similar considerations. The experimental results obtained by the writers, McLennan and McLeod,[5] and Wood[6] all support these theoretical conclusions.

In the present paper I want to report some experiments which I have been carrying on recently, and which show the relationship between Raman transitions and band spectrum structure much more clearly than before. A preliminary communication of these results has already been given in a letter to *Nature*,[1] but they were incomplete, and besides some inaccurate statements were made concerning the N_2 spectrum. Recently Wood[6] seems to have obtained similar results on HCl, in which the separation of rotational levels is large enough to be resolved with the low dispersion employed.

The essential improvement in the experimental arrangement consists in the use of the λ2536 mercury line as exciting light. The scattering is much stronger in that spectral region than in the visible, so that the Raman lines could be photographed with fairly large dispersion in a Hilger quartz spectrograph.

The primary source of light consisted of an especially built quartz lamp, about 25 cm. long and 2.5 cm. in diameter. The electrodes were water-cooled to keep the mercury vapor pressure low. In order to prevent too much reabsorption of the λ2536 radiation in the lamp itself, the discharge was bent toward the wall facing the tube with the scattering gas, by means of a properly designed electromagnet.

The lamp was used with a current intensity of 7 amp. The gases were contained in the tube at atmospheric pressure, and exposures of 60 to 120 hours were needed to get spectrograms of the scattered radiation.

The dispersion in the region of the λ2536 line was 129.7 frequency units per mm.

An iron arc spectrum was used as a standard. Working with a very narrow slit, perfectly sharp Raman lines were obtained, and their frequencies could be measured within a few tenths of a frequency unit.

The main result of these experiments has been to obtain well-resolved Raman lines corresponding to rotational transitions.

In the former paper, only the general consequences of the application

of the Kramers-Heisenberg formula to electronic and vibrational transitions in molecules were considered. Now we need to take into account also rotational states and electronic fine structure of molecular levels.

For our case, some general selection rules developed by Heisenberg,[7] Hund,[8] and Kronig[9] for molecular spectra are particularly useful.

Kronig deduces from the properties of symmetry of the eigenfunctions of diatomic molecules the general selection principle, that between any three terms in a molecular spectrum no more than two combinations can occur. Now, if we consider that for observing a transition $i \longrightarrow k$ in the Raman effect there must be at least a third state s such that the transitions $i \longrightarrow s$, $k \longrightarrow s$ occur in emission and absorption, we deduce from Kronig's rule the following general principle: only transitions between non-combining terms take place in the scattering process.

Of course, in the applications one has to be sure that the terms considered are really single; for instance, P terms are generally unresolved σ-type doublets, and each of the two components, which have different combination properties, has to be considered separately.

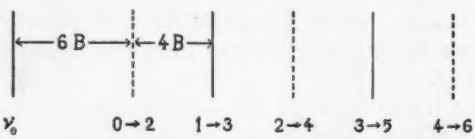


FIGURE 1

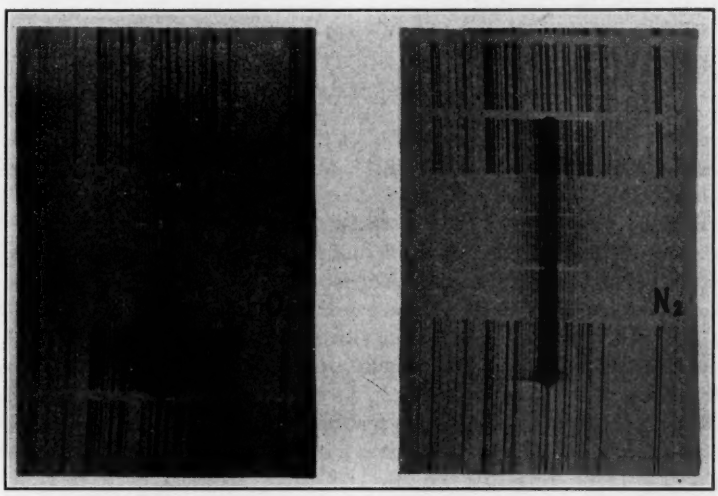
In the case of a symmetrical molecule, it has been shown by Heisenberg and Hund that the whole system of terms splits into two classes, according to the property of the total eigenfunction of being symmetrical or antisymmetrical in the coördinates of the nuclei. If the nuclei have no spin, only one of the two classes exists (the antisymmetrical class if the nuclei satisfy the Fermi-Pauli statistics, the symmetrical class if they satisfy the Einstein-Bose statistics). This is what happens, for instance, in O_2 and He_2.

The presence of a nuclear spin with different possibilities of orientation can make completely symmetrical or completely antisymmetrical the whole system of terms which was partly symmetrical and partly antisymmetrical before the introduction of the spin coördinates. Then both classes of terms exist, but they are practically non-combining, because of the extremely weak coupling between the nuclear spins. This behavior, similar to the splitting of the *He* terms in para- and ortho-terms, has been observed in N_2 and H_2.

The molecules so far investigated in the Raman effect are all in S states; therefore we will consider this case in detail from the theoretical standpoint. Mulliken's[10] notations will be used.

It has been shown by Hund[8] that in the case of S levels in a symmetrical molecule the successive rotational states belong alternatively to the two non-combining classes. If they have a fine structure (^2S, ^3S terms), all components having a common j_k and different values of j belong to the same class.

Now let us admit (as it will be justified later for the molecules actually investigated) that in the electronic bands to which the incoherent scattering is essentially due, besides the general selection rule $\Delta j = 0, \pm 1$ also $\Delta j_k = 0, \pm 1$ holds (which is true if the coupling between electronic orbital angular momentum, electronic spin and rotation is as in Hund's



Rotational Raman spectra in nitrogen and oxygen, showing the alternating intensities in N_2, due to the nuclear spin.

case b[8]). Then the transitions occurring in the scattering process must satisfy the condition $\Delta j_k = 0, \pm 2$. Considering pure rotational transitions, and neglecting the fine structure, the Raman shift is then given by

$$\pm\Delta\nu = F(j_k + 2) - F(j_k) = B(4j_k + 6),$$

where for a molecule with no nuclear spin j_k assumes either only odd or only even integral values; in the case of a nuclear spin, both.

The structure of this Raman spectrum is shown clearly in figure 1, where the full lines correspond to odd values of j_k, the dotted lines to even values.

After these considerations it is easy to understand the experimental results which I have obtained on O_2, N_2 and H_2.

Oxygen gives a pattern of equally spaced lines (six or seven of them are well measurable on each side of the exciting line; then they become very weak with increasing distance from the unmodified frequency, as it is to be expected from the Boltzmann factor.

The first one or two lines on each side cannot be measured as they overlap with the over-exposed image of the λ2536 line; but from the position of the other lines it is possible to show definitely that they constitute a pattern like that represented by the full lines in figure 1. That is, the distance of the nearest Raman line from the exciting line is $^{10}/_{8}$ times the other equal intervals (and not $^{6}/_{8}$ times as given by the pattern of the dotted lines, or $^{12}/_{8}$ as given by the complete pattern of both systems.) From this follows that only odd rotational levels are present.

This agrees with Ossenbrüggen's[11] analysis of the Schumann-Runge, $^3S \longrightarrow {}^3S$ absorption band system; and also the quantitative agreement is as good as it can be expected. From the measurements I get for the constant B (which is given by $^{1}/_{8}$ of the distance between consecutive Raman lines) the value 1.430 cm.$^{-1}$, as compared with Ossenbrüggen's value 1.439.

We may observe that the absorption bands which we must expect to take an essential part in the scattering process are the Schumann-Runge bands, as they are intense, and their frequency is not very far from that of the exciting light used. These bands satisfy the selection rule $\Delta j_k = 0, \pm 1$ as it must be for transitions between S states, which always fall under Hund's case b. So we should expect the rule $\Delta j_k = \pm 2$ to hold in this case in the scattering process.[12]

Nitrogen presents in the Raman spectrum the characteristic phenomenon of alternating intensities. The pattern is like in figure 1 with all the lines present. Those corresponding to transitions between even rotational states (dotted lines in the figure) are strong, the lines of the other system are weak.

This also fits with our knowledge of the N_2 spectrum. The normal state is a ^1S level,[13] so that here $j = j_k$, and the selection rule $\Delta j = 0, \pm 1$ allows only transitions with $\Delta j_k = \pm 2$ in the scattering process. Even and odd rotational states belong to two different non-combining classes, so that transition between consecutive levels are excluded.

The numerical value of B results to be 1.975 ± 0.01 cm.$^{-1}$. From this, the (hitherto unknown) moment of inertia of the nitrogen molecule in the normal state is found to be

$$I_0 = 14.0 \pm 0.1 \cdot 10^{-40}.$$

The considerations developed for N_2 hold also for H_2, which has also a nuclear spin and a normal ^1S level. I have been able to obtain in the Raman rotational spectrum only the transition $1 \longrightarrow 3$, which gives a line

displaced of 583 cm.$^{-1}$ from the exciting line. McLennan[5] has obtained also the weaker $0 \longrightarrow 2$ transition in liquid hydrogen. This shows, in conformity with Hori's[14] analysis of the absorption bands, that odd rotational states have a higher statistical weight in H_2.

Perhaps it is significant for the properties of the nuclei that N_2 and H_2, which have a similar electronic structure (^1S states), behave in opposite ways as to the relative weight of odd and even rotational states.

Most of what has been said about purely rotational transitions applies also to vibrational-rotational Raman spectra. In this case, for the molecules of the considered type, the Raman shift must be given, in first approximation, by

$$\Delta\nu_1 = \nu_0 + F(j_k) - F(j_k) = \nu_0$$
$$\Delta\nu_2 = \nu_0 + F(j_k + 2) - F(j_k) = \nu_0 + B(4j_k + 6)$$
$$\Delta\nu_3 = \nu_0 + F(j_k) - F(j_k + 2) = \nu_0 - B(4j_k + 6),$$

where ν_0 is the difference between the vibrational energies. We should have a Q-form branch, reduced to a single line, and PP- and RR-form branches. The coupling between rotation and vibration should separate the lines of the Q-form branch, and alter the spacing in the other branches.

So far only the unresolved Q-form branch has been observed. With the resolution available in the present experiments it actually shows an appreciable width. It is not surprising that the other branches should be missing, when we take into account that the Q-form branch is composed of something like ten or fifteen overlapping lines, and has on the plates just intensity enough to be observed. A line ten times weaker would certainly escape notice. Nevertheless I hope that further experiments will bring out the complete vibrational-rotational Raman bands.

The author wishes to express his indebtedness to the International Education Board for the award of a research fellowship at the California Institute of Technology.

[1] F. Rasetti, *Proc. Nat. Acad. Sci.*, **15**, 234, 1929; *Nature*, **123**, 757, 1929.
[2] E. C. Kemble and E. L. Hill, *Bull. Phys. Soc.*, Apr., 1929; these PROCEEDINGS, **15**, 387, 1929.
[3] R. M. Langer, *Nature*, **123**, 345, March 9, 1929.
[4] G. H. Dieke, *Ibid.*, **123**, 564, Apr. 13, 1929.
[5] J. C. McLennan and J. H. McLeod, *Nature*, **123**, 160, 1929.
[6] R. W. Wood, *Bull. Phys. Soc.*, Apr., 1929; *Phil. Mag.*, **7**, 744, 1929.
[7] W. Heisenberg, *Zeits. Phys.*, **41**, 239, 1927.
[8] F. Hund, *Ibid.*, **40**, 742, 1927; **42**, 93, 1927.
[9] R. de L. Kronig, *Ibid.*, **46**, 814, 1927.
[10] R. S. Mulliken, *Phys. Rev.*, **30**, 785, 1927; **32**, 388, 1928.
[11] W. Ossenbrüggen, *Zeits. Phys.*, **49**, 167, 1928.
[12] Otherwise also $\Delta j_k = \pm 4$ and $\Delta j_k = \pm 6$ could be possible.
[13] R. S. Mulliken, *Phys. Rev.*, **32**, 86, 1928.
[14] T. Hori, *Zeits. Phys.*, **44**, 834, 1927.

ON THE THEORY OF ELECTRON SCATTERING IN GASES

By Allan C. G. Mitchell

Bartol Research Foundation of the Franklin Institute

Communicated May 11, 1929

A general wave-mechanical theory of collisional processes has been developed by Born[1] and applied by Wentzel[2] to the scattering of alpha particles by heavy atoms and by Elsasser[3] to collisional processes in atomic hydrogen. Recently Sommerfeld[4] has applied the method to the general problem of scattering and has found agreement with the experimental results.

To carry out the calculation it is necessary to know the potential of the atom as a function of the distance from the nucleus. Wentzel first assumed the potential of an atom of atomic number Z to be given by the Coulomb law $v(r) = Ze/r$, neglecting the effect of the electrons around the nucleus but found that this lead to integrals which would not converge. On assuming the potential function to be $v(r) = Ze/r\, e^{-\frac{r}{R}}$, where R is of the order of magnitude of an atomic radius, he was able to obtain a scattering formula which, for alpha-particles, agreed with the Rutherford scattering law. On the other hand, Elsasser found the potential of the hydrogen atom in terms of its eigenfunctions, the potential of the hydrogen atom in its normal state being similar to that used by Wentzel, thus justifying his assumption, and showed that a scattering law could be obtained. Finally, Sommerfeld considered scattering from other atoms by treating all the electrons of the atom as united in the K-shell without mutually influencing each other. "The action of these electrons toward the outside would then be represented wave-mechanically by the Z-fold electron cloud of hydrogen in its normal state" and the potential energy of an electron in the field of the atom by

$$V(r) = -e^2Z(1/r + Z/a)e^{-2r\frac{Z}{a}} \qquad (1)$$

where a is the radius of the first Bohr circle. By using this potential energy in the Born collision equations he arrived at a scattering formula, which for high velocity alpha-particles and for not too small scattering angles, agrees with the Rutherford scattering law. The formula also agrees with the experiments of Kirchner[5] on the scattering of electrons in argon (elastic collisions). It will be noted that expression (1) for the potential energy takes into account shielding by the electrons of the atom.

It is the purpose of this paper to carry through the calculations using a somewhat different method of obtaining the potential function for the atom. Fermi[6] and Thomas[7] have shown that if the electrons of an atom

of atomic number Z be considered to be a perfectly degenerate gas in the sense of the Fermi statistics, the potential at a distance r from the nucleus will be given by

$$v = Ze/r\Phi\left(\frac{r}{\mu}\right)$$

where

$$\mu = \frac{3^{2/3}\,\mathrm{h}^2}{2^{13/3}\,\pi^{4/3} me^2 Z^{1/3}}. \tag{2}$$

The function $\Phi(\frac{r}{\mu})$ is unity when r is zero and decreases to zero for increasing r, such that for distances a little greater than the atomic radius the potential will be practically zero. No analytical expression is known for the function over its whole range but a table of values is given by Fermi (loc. cit.). In this paper we shall consider this potential function as giving the true potential of the atom, inclusive of shielding, and use the potential energy derived therefrom in conjunction with the Born Collision Theory to calculate the scattering from different atoms.

We follow Born, using however the Sommerfeld notation (loc. cit.). A plane wave for an electron approaches the atom from the negative X-direction. The wave equation for the total system, electron plus atom, is

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0. \tag{3}$$

We consider V, the potential energy of the system, as a perturbation term and write

$$\psi = \psi_0 + \psi_1 + \ldots \tag{4}$$

Substituting in (3), writing $k^2 = \frac{8\pi^2 mE}{h^2}$, and neglecting $V\psi_0$ in comparison to ψ_0 and $\Delta^2\psi_0$, we arrive at the set of equations

$$\nabla^2\psi + k^2\psi_0 = 0 \tag{5}$$

$$\nabla^2\psi_1 + k^2\psi_0 = k^2\frac{V}{E}\psi_1. \tag{6}$$

For the oncoming electron wave we have the solution

$$\psi_0 = e^{ikx}. \tag{7}$$

Making the usual application of Green's theorem we obtain for the solution of the inhomogeneous equation (6)

$$\psi_1 = -\frac{k^2}{4\pi E}\int V(r_Q)\,\frac{e^{ikr_{PQ}}}{r^{PQ}}\,e^{ikx_Q}\,d\tau' \tag{8}$$

in which we neglect terms of lower order than ψ_1. In this notation the atom is at a point O, the scattering is observed at a point P at a distance $OP = r$ from the atom. Equation (8) gives the number of waves scattered from a volume element $d\tau'$ situated at a point Q, at a distance r_Q from the atom and r_{PQ} from the point P. The integral is to be taken over all space. We consider the distance r, from atom to observer to be large compared to that over which scattering takes place (r_Q of the order of an atomic radius). Taking $\mathbf{e}$ and $\mathbf{e}_0$ as unit vectors in the directions r and X, respectively, we have, to a first approximation

$$r_{PQ} = r - \mathbf{e} \cdot \mathbf{r}_Q \; ; x_Q = \mathbf{e}_0 \cdot \mathbf{r}_Q$$

and hence (8) becomes

$$\psi_1 = -\frac{k^2}{4\pi E}\frac{e^{ikr}}{r}\int V(r_Q)e^{ik(\mathbf{e}_0-\mathbf{e})\cdot \mathbf{r}_Q}\, d\tau'. \qquad (9)$$

We now choose a system of polar coördinates such that the polar axis is parallel to $(\mathbf{e}_0 - \mathbf{e})$, and take

$$r_Q = \rho \; ; (\mathbf{e}_0 - \mathbf{e}) \cdot \mathbf{r}_Q = |\mathbf{e}_0 - \mathbf{e}|\, \rho \cos\theta.$$

The scattering angle Θ is that between OX and OP, then

$$|\mathbf{e}_0 - \mathbf{e}| = 2 \sin\frac{\Theta}{2}.$$

We further introduce for V the potential energy of an electron in the field of an atom derived from the Fermi statistics

$$V(\rho) = -\frac{Ze^2}{\rho}\Phi\frac{\rho}{\mu}.$$

Making the above substitutions (9) becomes

$$\psi_1 = -\frac{k^2}{4\pi E}Ze^2\frac{e^{ikr}}{r}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\Phi\left(\frac{\rho}{\mu}\right)e^{i2k\rho \sin\Theta/2}\,\rho d\rho \sin\theta d\theta d\phi. \qquad (10)$$

Integrating with respect to ϕ and then to θ we obtain

$$\psi_1 = \frac{k^2}{2E}\frac{Ze^2}{r}e^{ikr}\frac{1}{\sin\Theta/2}\int_0^{\infty}\Phi\left(\frac{\rho}{\mu}\right)\sin(2k\,\rho\sin\theta/2)\,d\rho. \qquad (11)$$

We now form the quotient $\left|\frac{\psi_1}{\psi_0}\right|^2$ and remembering $|\psi_0|^2 = 1$ we obtain

$$P = \left|\frac{\psi_1}{\psi_0}\right|^2 = \left[\frac{k\,Ze^2}{E2r}\right]^2\frac{1}{\sin^2\Theta/2}\left[\int_0^{\infty}\Phi\left(\frac{\rho}{\mu}\right)\sin(2k\,\rho\sin\Theta/2)d\rho\right]^2. \qquad (12)$$

This last equation may be interpreted as giving the number of scattered particles crossing a unit area per unit time at a distance r from the atom and at an angle Θ to the oncoming electron beam, in relation to the number of particles per unit area striking the atom. The particles are scattered without loss of velocity.

We shall now compare this with the following expression obtained by Sommerfeld

$$P = \left[\frac{Ze^2}{4Er}\right]^2 \left[\frac{1}{\sin^2 \Theta/2 + \alpha^2} + \frac{\alpha^2}{(\sin^2 \Theta/2 + \alpha^2)^2}\right]^2 \qquad (13)$$

where $\alpha = \dfrac{Z}{ak}$.

The above formula gives the Rutherford scattering law for alpha-particles if we neglect α^2 in comparison to $\sin^2 \Theta/2$ and if we introduce the proper factor into the constant to take care of the double charge of the alpha-particle. It has been shown that for alpha-particles the factor α^2 may be neglected in comparison to $\sin^2 \Theta/2$ for not too small angles of scattering. On the other hand equation (13) gives for $\Theta = 0$.

$$P = \left[\frac{Ze^2}{4Er}\right]^2 \frac{4}{\alpha^4} \qquad (14)$$

i.e., a finite number of particles scattered at $\Theta = 0$ instead of an infinite number as given by the Rutherford law. That the number of electrons scattered at $\Theta = 0$ in argon is not infinite but is given by (14) in agreement with Kirchner's experiments is shown by Sommerfeld.

It remains to investigate whether our expression (12) leads to a finite number of particles scattered at $\Theta = 0$ and if so whether this number agrees with that calculated from (14). Putting $\Theta = 0$ into (12) leads to an indeterminate form which is easily evaluated and gives

$$P_{\Theta=0} = 4k^4 \left[\frac{Ze^2}{2Er}\right]^2 \left[\int_0^\infty \rho \Phi\left(\frac{\rho}{\mu}\right) d\rho\right]^2. \qquad (15)$$

We write $x = {}^{\rho}/_{\mu}$ and obtain

$$P_{\Theta=0} = 4k^4\mu^4 \left[\frac{Ze^2}{2Er}\right]^2 \left[\int_0^\infty x\Phi(x)dx\right]^2. \qquad (16)$$

A graphical integration of the function under the integral[8] leads to a definite value and hence the right hand side of (16) is finite, in agreement with (14). By applying the usual criteria for maxima and minima to equation (12), it is easy to show[9] that the scattering is a maximum at $\Theta = 0$ and a minimum at $\Theta = \pi$, in agreement with Sommerfeld's theory.

A comparison of the amount of scattering at different scattering angles computed on the basis of the different theories may be obtained as follows. Making the substitution $x = {}^{\rho}/_{\mu}$, equation (12) becomes

$$P = \left[\frac{Ze^2}{2Er}\right]^2 \frac{k^2\mu^2}{\sin^2 \theta/2}\left[\int_0^\infty \Phi(x) \sin(2k\mu x \sin \theta/2)dx\right]^2. \quad (17)$$

We now arbitrarily take the factor $\left[\frac{Ze^2}{2Er}\right]^2$, occurring in both theories, equal to unity, and compare the results obtained from (17) with those obtained from (13), using suitable values for the constants occurring in the equations. The integration of (17) is carried out graphically with the help of Fermi's tables for $\Phi(x)$ by plotting $\Phi(x) \sin(2k\mu x \sin \theta/2)$ against x and computing the area under the curve. On account of the sine function occurring in the integral the curve is an oscillatory one, and since $\Phi(x)$ decreases rather rapidly with x, it is found unnecessary to go to values of x beyond $x = 10$, since the contribution to the integral beyond that point is small compared to that for smaller x. The results obtained for 15 k.-v. electrons in argon ($\mu = 1.79 \times 10^{-9}$, $\alpha = 0.3$, $k = 6.28 \times 10^9$) and for 120-volt electrons in the same gas ($\mu = 1.79 \times 10^{-9}$, $\alpha^2 = 38.4$, $k = 5.5 \times 10^8$) are given in table 1. The results obtained from the Rutherford law are also tabulated.

TABLE 1

RELATIVE SCATTERING PER UNIT SOLID ANGLE

	RELATIVE SCATTERING		
θ	RUTHERFORD	MITCHELL	SOMMERFELD
	15 K.-v. Electrons in Argon		
0	∞	1.6×10^6	9.0
45	12.0	11.0	3.1
90	1.0	0.5	0.2
	120-Volt Electrons in Argon		
0	∞	100	6.8×10^{-4}
45	12.0	1.6	6.7×10^{-4}
90	1.0	0.4	6.5×10^{-4}

It will be seen that the scattering formula derived on the basis of the Fermi statistical potentials gives rise to greater scattering than does the Sommerfeld formula, but to less than does the Rutherford formula. The fact that this theory gives relative scattering lying between the Rutherford theory and the Sommerfeld theory is due to the form of potential function chosen and its connection with the manner in which we calculate the shielding of the outer electrons. On the Rutherford theory we consider a "naked nucleus;" on the Sommerfeld theory we consider an exceptionally well-shielded nucleus due to the assumption that all the electrons are in the K-shell; and, finally, on the present theory we prob-

ably have less efficient shielding since the assumption of the Fermi potentials is equivalent to assuming a more or less uniform distribution of electrons throughout the whole atom.

We believe the old method of assuming all the electrons of an atom to be concentrated in the K-shell to be somewhat illogical in the light of our knowledge of the periodic table. On the other hand, the argument presented in this paper appears to be logical insofar as the calculation of atomic fields by the method of Fermi is logical. The latter, however, seems to be in agreement with the laws of the periodic system since Fermi has used it to calculate in which atoms the s, p, and d terms appear and has found agreement with the facts.

In conclusion the writer to acknowledge his indebtedness to his colleagues of the Bartol Research Foundation, in particular to Prof. W. F. G. Swann and Dr. A. Bramley, for many helpful suggestions in connection with the work.

Summary.—The scattering of electrons in gases has been treated using the Born collision theory in connection with the Fermi statistical potential for atomic fields. The general theory has been given and, in particular, the relative number of electrons scattered at several angles in argon has been calculated and shown to be greater than that obtained on the basis of the Sommerfeld theory but less than on the Rutherford theory.

[1] M. Born, *Zs. Phys.*, **37**, 863 (1926); **38**, 803 (1926).

[2] G. Wentzel, *Ibid.*, **40**, 590 (1927).

[3] W. Elsasser, *Ibid.*, **45**, 522 (1927).

[4] A. Sommerfeld, *Atombau und Spektrallinien*, Wellenmechanischer Ergänzungsband, p. 226 et seq.

[5] F. Kirchner, *Ann. Phys.*, **83**, 969 (1927).

[6] E. Fermi, *Zs. Phys.*, **48**, 73 (1928).

[7] L. H. Thomas, *Proc. Camb. Phil. Soc.*, **23**, 542 (1926).

[8] The integration was carried out by using the values of $\Phi(x)$ for $x = 0$ to $x = 20$ as given by Fermi in his table, and taking the area under the curve $x\Phi(x)$ against x. Since the exact form of $\Phi(x)$ is not known the integration of $\int_{20}^{\infty} x\Phi(x)d$ could not be carried out precisely. The approximate form of $\Phi(x)$ can be obtained and it can be shown that $\int_{20}^{\infty} x\Phi(x)dx$ converges, the value of this integral being less than half the value of the integral from 0 to 20.

[9] For a detailed account see a paper by the author which will appear shortly in the Journal of the Franklin Institute.

MOLECULAR BINDING AND LOW ^5S TERMS OF N^+ AND C

BY LOUIS A. TURNER

PALMER PHYSICAL LABORATORY, PRINCETON UNIVERSITY

Communicated April 20, 1929

The extensive analysis of the negative bands of nitrogen by Herzberg[1] led to the conclusion that it requires more energy to dissociate an N_2^+ ion in the normal state by increase of its vibrational quantum number than it does first to excite it to the upper electronic state involved in the emission of the negative bands and then dissociate it by increase of the vibrational quantum number. This suggested that the dissociation of the *excited* molecular ion produces a normal atom and a normal atomic ion, whereas the dissociation of the *normal* molecular ion produces an atom and an ion, one of which is excited. The energy difference is 2.4 volts. Since the energy of the nitrogen atom in the $(2s)^2(2p)^3\ ^2D$ state is 2.38 volts[2] with respect to the normal $(2s)^2(2p)^3\ ^4S$ state the assumption that the normal molecular ion dissociates into a normal ion and an excited atom is made. Heitler and Herzberg[3] have recently pointed out the analogous relations between the energy levels of CN and SiN, and have shown that the energy differences involved for those molecules are definitely less than 2.4 volts and cannot be attributed to energy of excitation of an N atom. The other atom must be the one which is excited and so, by analogy, one would expect the N^+ ion to be excited rather than the N atom, the agreement of the energy of 2.4 volts with that of the energy of excitation of an N atom being fortuitous. They suggest that the excited state of N^+, C and Si is the $2s(2p)^3\ ^5S$ state, the higher multiplicity corresponding to higher valence and increased energy of binding with the N atom, in accord with the newer theories of valence.

This $2s(2p)^3\ ^5S$ term, however, is one which should combine with the normal $(2s)^2(2p)^2\ ^3P$ term of N^+ which has been located by Bowen.[4] There should be two lines having a $\Delta\nu$ of 831, the difference between the $^3P_2$ and $^3P_1$ levels, and in the neighborhood of 5100 A.U., the wave-length corresponding to 2.4 volts. Inspection of the table of NII lines given by Fowler and Freeman[5] shows the following pair with the correct $\Delta\nu$:

INT.	λ	ν	
2	4991.22	20029.61	
			$\backsim$ 2.48 volts
2	5012.026	19946.46	
		83.15	

Since the number of unidentified lines of NII in this region of the spectrum is small, the chance that this is an accidental agreement is corre-

spondingly small. These lines should be weak as are other intercombinations lines in the spectra of light atoms. The ^5S term, being the lowest possible quintet term, would, however, be expected to give stronger intersystem lines by combination with the only lower term with which it can combine, viz., ^3P, than higher quintet terms which can combine with other lower quintet terms rather than with triplet terms. Such low intersystem combinations have been found to be present in the spectra of other light atoms (e.g., $(2s)^2(2p)^5\ ^2P - (2s)^2(2p)^6\ 3s\ ^4P$ of Ne^+).[6]

The corresponding energy difference for C is 1.6 ± 0.3 volts so that the lines should be found between 6500 and 9500 A.U. with a $\Delta\nu$ of 27.5, the latter from combinations with the normal ^3P term found by Bowen. No such lines appear in the list of Ryde[7] or in the list of unclassified lines given by Fowler and Selwyn.[8] The spectrum of Si is not well enough known for such a comparison to be made.

If this placing of the ^5S term by Heitler and Herzberg be accepted, whether or not the spectroscopic support here adduced be considered as convincing, an apparent difficulty arises in the fact that the energy of this state is so tremendously different from that of the other states arising from the same electronic configuration. The configurations and resulting terms by Hunds theory are as follows:

$(2s)^2(2p)^3$ N	^4S		^2D		^2P	
$2s(2p)^3\ N^+$	^5S	^3S	^3D	^1D	^3P	^1P

The ^3D and ^3P terms of N^+ were found by Bowen and lie 11.4 and 13.5, respectively, above the normal $(2s)^2(2p)^2\ ^3P$ term. The ^3S suggested was still higher (19.2 volts), which seemed curious because the ^4S of the $2p^3$ configuration with which it is built lies below the ^2D and ^2P with which the ^3D and ^3P are built. Perhaps there is some sort of a strong resonance coupling of the $2s$ electron with the $(2p)^3\ ^4S$ group, the ^3S term being very high and the ^5S very low. There is, however, some doubt about the identification of the lines attributed to a combination with this ^3S term by Bowen. Compton and Boyce[2] found their behavior to be unlike that of others of Bowen's lines, Fowler and Selwyn[8] give a considerably different value for the term without giving the data from which it was calculated. The energies of the corresponding ^3D and ^3P states of C with respect to the normal are 7.9 and 9.3 volts, respectively.

The wave-lengths of these $^3P - {}^5S$ lines of N^+ given by Heitler and Herzberg's theory are considerably larger than those predicted by the author[9] by a rather indirect and uncertain calculation.

The correct fixation of these ^5S terms, especially those of C and Si, is of importance because it will give support for the theory of London and Heitler[10] of the quadrivalence of these atoms if they are found to be very

low and will present a serious difficulty if they are found to be high. These results with N^+ indicate that they are low.

[1] G. Herzberg, *Ann. d. Phys.*, **86**, 189, 1928; *Nature*, **122**, 505, 1928.
[2] K. T. Compton and J. C. Boyce, *Phys. Rev.*, **33**, 145, 1929.
[3] W. Heitler and G. Herzberg, *Z. Physik*, **53**, 52, 1929.
[4] I. S. Bowen, *Phys. Rev.*, **29**, 231, 1927.
[5] A. Fowler and L. T. Freeman, *Proc. Roy. Soc.*, **114A**, 662, 1927.
[6] H. N. Russell, K. T. Compton and J. C. Boyce, *Proc. Nat. Acad. Sci.*, **14**, 280, 1928.
[7] J. W. Ryde, *Proc. Roy. Soc.*, **117A**, 164, 1927.
[8] A. Fowler and E. W. H. Selwyn, *Ibid.*, **118A**, 34, 1928.
[9] L. A. Turner, *Phys. Rev.*, **32**, 727, 1928.
[10] F. London, *Z. Physik*, **46**, 455, 1928; W. Heitler, *Ibid*, **47**, 835, 1928.

Note Added with Proof May 25, 1929.—Professor H. N. Russell suggested that if this identification of the two NII lines be correct they should appear as nebular lines and in the spectra of some of the hot stars in which other NII lines are found. They are not given in the published lists of nebular lines. Dr. W. S. Adams of the Mount Wilson Observatory has kindly looked for them in the stellar spectra and finds no certain evidence of their presence. This suggested classification is thereby made extremely doubtful.

WAVE-LENGTH OF THE K LINES OF COPPER USING RULED GRATINGS

By J. A. Bearden

Ryerson Physical Laboratory, University of Chicago

Communicated May 13, 1929

Ruled gratings have been used by several experimenters[1] to determine the absolute wave-length of x-ray spectrum lines. The importance of measuring x-ray wave-lengths by this method is that a standard of x-ray wave-lengths may thus be established which should be more reliable than those resulting from crystal measurement. From the wave-lengths thus obtained one may calculate the crystal grating space and the fundamental constants N and e. Since Planck's constant h varies with e one obtains also a new value for this constant.

Theory.—The wave-length of the x-rays can be obtained from the ordinary optical diffraction formula, which can be written in the form,

$$N\lambda = D\left\{\cos\theta - \cos(\theta + \alpha)\right\}, \tag{1}$$

$$= D\left(\alpha\theta + \frac{\alpha^2}{2} - \ldots\right), \tag{2}$$

to a close approximation, where θ is the glancing angle of incidence, $(\theta + \alpha)$ the glancing angle of diffraction for the nth order, and D is the

grating space of the grating. The angles θ and α may be determined by the method of using two plates as shown in figure 1. Theoretical calculation of the probable errors entering into the various methods of measuring angles shows this method to be the most accurate. For this case equation (2) may be written in terms of the measured quantities

$$\lambda = \frac{D}{2b^2}\left\{\frac{(y-x)^2\,(y \pm z)z}{y^2}\right\}, \qquad (3)$$

where the $+z$ refers to the outside orders of diffraction and $-z$ to the inside orders.

Experiment.—The source of x-rays was a water-cooled copper target Coolidge tube with a thin window (0.01 mm. aluminum) to reduce the absorption of the radiation. The K lines of copper were chosen for the experiment because they are the longest intense x-ray lines which can be used without a vacuum spectrograph, and since their wave-lengths can

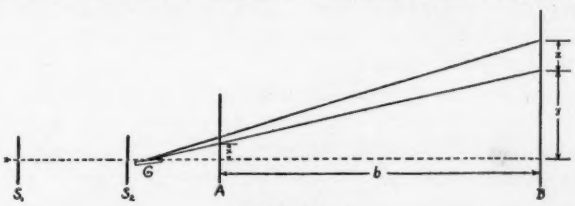


FIGURE 1

be used to determine directly the grating spaces of calcite and rock salt. The tube was run at 35 ma. and 50 kv. The absorption of the x-rays in air through the 270-cm. distance from the tube to the plate B was reduced by placing an evacuated tube between the slits S_1 S_2 and another between the grating and the plate B. The ends of the tubes were closed with very thin celluloid.

The direct rays from the tube were collimated by gold-faced slits S_1 and S_2 which were 0.01 mm. wide and 50 cm. apart. They were adjusted parallel with the surface of the grating to within 10 seconds of arc. The grating was mounted on a micrometer slide placed on the table of a precision Geneva spectrometer. The grating was centered on the axis of rotation and its surface made parallel with the axis of rotation by a modified Michelson interferometer. By observing the interferometer during the exposure a possible shift of the grating as small as 0.1 of a white-light fringe or a rotation of 1 second of arc could be detected. The plate holders A and B were about 2 meters apart and were adjusted perpendicular to the direct x-ray beam to within 5 seconds of arc by the use of a telescope and Gauss eyepiece.

The distance between the plates A and B was measured by placing

between the plates an iron rod about 190 cm. long whose ends were parallel, and then measuring with inside micrometers the distance between the ends of the rod and the plates. The length of the bar was determined by comparison with the laboratory standard. The error in measuring this distance b was estimated to be less than 0.04 mm. In order to avoid uncertainties in the planeness of the plates, they were made of selected plate glass, coated with Eastman x-ray emulsion. The distances between the lines on the plates were measured with a Gaertner comparator. The entire apparatus was mounted on a cast iron slab 9 ft. long, 2 ft. wide and 5 in. thick.

A glass grating of 600 lines per mm. and a glass and a speculum metal grating, each with 50 lines per mm., were kindly ruled for this work by Mr. Pearson, under the direction of Professor Michelson. The grating space was checked, using the green line of mercury as a standard. It was found possible to increase the critical angle θ by coating the surface of the grating with gold or platinum. This did not increase the precision of the experiment, however, because the lines were not as sharp at large angles θ as at smaller angles.

In exposing a series of plates the grating was first withdrawn from the path of the x-rays by means of the micrometer slide, and the direct beam recorded on plate B by a short exposure. Plate A was then inserted and the direct beam registered. The grating was next moved into position, and the reflected beam recorded on plate A. This plate was then removed and a long exposure, usually about 24 hours, given to record the reflected beam and the various orders of the spectrum on plate B. In order to make sure that nothing had happened to change the adjustments, a new plate B' was now inserted in place of B, a short exposure given to record the reflected beam, the grating withdrawn, and the direct beam recorded. It was difficult to get plates B and B' to check accurately, though when the room temperature was controlled to within 0.2 degrees C., this trouble was no longer serious.

Results.—Typical plates are shown in figure 2. Plates a and b are taken at different angles θ with the 50-line glass grating, c is a plate using the speculum grating used by Wadlund, and d is a plate using the 600-line glass grating. The exposures were all about 24 hours. Thirty-one plates have been taken under various conditions. Using the 50-line glass grating twelve orders have been obtained on several plates, but with the speculum grating only about seven orders have been obtained with a 36-hour exposure. With the 600-line glass grating it does not seem possible to get more than 2 orders even with a 72-hour exposure, but the first and second order are measurable with an 18-hour exposure. It has not been possible to separate the α_1 and α_2 lines even in the highest orders obtained. A broadening of the lines is noticed in the second order from the 600-line

glass grating and in the eighth to the twelfth orders of the 50-line glass grating.

In some of the exposures the difference between plates B and B' was rather great, indicating a motion of the apparatus during the exposure. It was therefore decided that the most reliable result would be obtained by selecting out of the 31 plates the 10 showing the least indication of motion and taking the measurements from these. The weighted mean of these 10 plates gives*

$$K_\alpha = 1.5422 \pm 0.0002 \text{ Å}$$
$$K_\beta = 1.3926 \pm 0.0002 \text{ Å}.$$

Every one of the 31 plates obtained from these three gratings gave wavelengths greater than those calculated from crystal diffraction data.

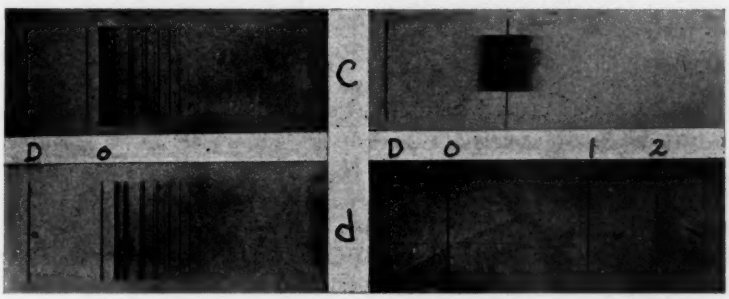


FIGURE 2

D and O are short exposures of the direct beam and the directly reflected beam, respectively. The edge between the line O and the first order is the edge of a lead screen which shielded the plate during most of the long exposure so that the directly reflected beam would not be over exposed. On plate C a diaphram was used to shield the plate at the top and bottom instead of placing a shield first over the O line.

In order to compare the lines here obtained with the crystal measurements, one must take a weighted mean of the α_1 and α_2 lines as given by the crystal measurements. If we assume a form of the lines of the type $y = e^{-x^2}$, it can be shown that the maximum intensity of the unresolved doublet should occur very near the "center of gravity" of the two lines. Siegbahn's value[2] of the α line as thus weighted is 1.5386 Å. The measurements on the β line do not involve this difficulty since it is resolved only with difficulty even by the crystal grating. Siegbahn gives for the copper $K\beta$ line, $\lambda = 1.3893$ Å. For both the α and the β lines the present values from the ruled gratings are 0.23 per cent higher than the crystal values given by Siegbahn.

This result is so different from what had been expected as to suggest a hidden error, and for that reason publication has been withheld for several months. In an effort to discover such an error, an independent set of measurements was made by Professor Compton with results confirming those of the writer. Since Wadlund[1] had obtained results agreeing with the crystal measurements, a new determination was made using the same grating as that employed by Wadlund. The results were consistent with the writer's measurements with his other gratings, and apparently of a higher order of precision than Wadlund's determination. No source of error has been found that would account for more than a very small fraction of the difference between my measurements and those by the crystal methods.

Using these values of the wave-length one finds the grating space of calcite to be 3.035 Å, Avogadro's number as $N = 6.022 \times 10^{23}$ per gram molecule, and the electronic charge $e = 4.804 \times 10^{-10}$ e. s. u. Since, according to Birge, Planck's Constant varies as $e^{1.24}$ one obtains a value $h = 6.604 \times 10^{-27}$ erg sec. Using these values one obtains for the fine structure constant $1/\alpha = 136.6$, which still differs considerably from the theoretical value 136 assigned by Eddington.[3] By using the value of e/m as determined from deflection experiments one gets a value of the Rydberg Constant, which is about 0.4 per cent too high.

It is not possible to account for these differences as due to a lack of homogeneity in the crystal, as suggested by Joffe[4] and Zwicky,[5] for gaps in the crystal such as they assume would result in even larger differences than those observed. Two other suggestions occur: First, the very unlikely chance that the diffraction formula may not hold for these wave-lengths. Second, an index of refraction might conceivably have some effect upon the wave-length as determined by this method. The fact that the results from the speculum grating, the gold-coated grating, and the glass gratings in all orders are consistent with each other, however, seems to rule out these possibilities.

A confirmation of these results is obtained in the recent work of Howe.[6] He finds for the L series from 10 to 40 Å a considerably higher value for these lines than is given by crystal measurements.

Further measurements are in progress and it is hoped that other wave-lengths can be used so that a system of standards can be obtained which are more accurate than can be obtained by crystal measurements.

The writer wishes to express his appreciation to Professor Compton for his interest and coöperation in the work.

[1] A. H. Compton and R. L. Doan, *Proc. Nat. Acad. Sci.*, **11**, 598 (1925). Thibaud, *Comptes Rendus*, Jan., 1926. Osgood, *Phys. Rev.*, **30**, 567 (1927). Hunt, *Ibid.*, **30**, 227 (1927). Weatherby, *Ibid.*, **32**, 707 (1928). Bäcklin, Qnaugurald Dissertation, Uppsala Universitets, Arsskrift, 1928. Wadlund, *Phys. Rev.*, **32**, 841 (1928). Söderman, *Zeit. Phys.*, **52**, 795 (1929). Howe, *Proc. Nat. Acad. Sci.*, **15**, 251 (1929).

[2] Siegbahn, *The Spectroscopy of X-Rays*, **1925.**
[3] Eddington, *Proc. of the Royal Soc.*, Jan., 1929.
[4] Joffe, *The Physics of Crystals*, pp. 56–66, 1926.
[5] Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253 (1929).
[6] Howe, *Proc. of Am. Phys. Soc.*, (Washington Meeting, 1929).

* *Note Added in Proof.*—The values given here are lower than those reported at the Washington Meeting of the American Physical Society in April, 1929. This is due primarily to a difference between the scale of the two comparitors used in measuring the plates and the laboratory standard decimeter calibrated by the Bureau International des Poids et Measures.

EFFECT OF VOLUME CHANGES ON THE INFRA-RED VIBRATIONS OF SIMPLE CRYSTALS

BY E. O. SALANT*

DEPARTMENT OF PHYSICS, WASHINGTON SQUARE COLLEGE,
NEW YORK CITY

Communicated April 30, 1929

Reasoning from the Born lattice theory, Born and Brody[1] first derived relations between the vibration frequencies in simple crystals of the sodium chloride type and the law of force between the ions in the crystal. This law is supposed to vary as the inverse nth power of the distance between the ions, acting in an opposite sense to that of the Coulomb forces. Using the value of n obtained from compressibility data, calculated values of the residual ray frequencies agreed quite well with measured values.

Starting from this theory, Zwicky[2] derived a relation for the effect of uniformly applied pressure on the vibration frequencies. Some time previously, Grüncisen,[3] in his studies of monatomic solids, had shown how their vibration frequencies might be expected to vary as the volume of the solid changed, the variation being related to the laws of attraction and repulsion of the atoms.

Recently, Carpenter and Stoodley[4] have related the law of force to the vibration frequencies of sodium-chloride type crystals in an extremely simple manner. The result of their method—which it is unnecessary to describe here—is that the vibration frequency may be written

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{m_1 + m_2}{m_1 m_2}\frac{2b_n}{r^{n+1}}(n-2)\left(1+\frac{4}{3^{\frac{n+2}{2}}}\right)}, \qquad (1)$$

where m_1 and m_2 are the masses of the cation and anion, b_n the elastic constant and r is the lattice spacing, the distance apart of neighboring ions in the crystal.

Suppose, now, that we study the effect of changing this distance apart, that is, the volume, on the vibration frequency. We have, then,

$$\frac{d\nu_0}{dr} = \frac{1}{2\pi}\sqrt{\frac{m_1 + m_2}{m_1 m_2}\frac{2b_n}{r^{n+3}}(n-2)\left(1 + \frac{4}{3^{\frac{n+3}{2}}}\right)}\left(-\frac{n+1}{2}\right)$$

which, using (1), becomes

$$\begin{cases} \dfrac{d\nu_0}{dr} = -\dfrac{n+1}{2}\dfrac{\nu_0}{r} \\ \dfrac{d\lambda_0}{dV} = \dfrac{n+1}{6}\dfrac{\lambda_0}{V} \end{cases} \tag{2}$$

where V is the molal volume of the crystal and λ_0 is the wave-length corresponding to ν_0. Thus, measurements of the vibration frequencies at various volumes would lead to direct and independent information about n, the index of the law of force.

The changes of volume will, of course, be brought about by variations of temperature and of pressure. For temperature changes,

$$\left(\frac{\partial\lambda_0}{\partial T}\right)_P = \frac{n+1}{6}\lambda_0\alpha, \tag{3}$$

where α is the coefficient of thermal expansion; for pressure changes,

$$\left(\frac{\partial\lambda_0}{\partial P}\right)_T = \frac{n+1}{6}\lambda_0\chi \tag{4}$$

where χ is the volume compressibility.

In table 1 are the changes in λ_0 calculated for several crystals due to 100°C. or 100 atmospheres change, together with the data for the calculations.

TABLE 1

VARIATION OF λ_0 WITH TEMPERATURE AND PRESSURE

SALT	(1) λ_0	(6) n	(8) α	(8) χ	$\pm\Delta\lambda_0$ FOR $\pm\Delta$ 110° C.	$-\Delta\lambda_0$ FOR 100 ATMOSPHERES
NaCl	66.7	10	1.1	4.12	1.35	0.052
KCl	78.0	9	1.0	5.52	1.30	0.074
XBi	94.0	9	1.1	6.57	1.72	0.11
KI	115.0	10	1.25	7.78	2.64	0.17

When it is recalled that the temperature can be conveniently lowered 200°, and raised some 600° above room temperatures before the salts melt, it is obvious that the temperature shifts of λ_0 should be quite easily measurable. The pressure shifts will, naturally, be more difficult, as transparent windows that can withstand large pressures will be required. Both these shifts in λ_0 are determined, strictly, from the changes in the dispersion curve.

The Havelock equation[5] relates the natural frequencies of vibration to the maxima of the residual rays by means of the dielectric constants:

$$\lambda_m = \frac{\lambda_0}{\sqrt{1 + \frac{K}{6\epsilon - 6K - 4}}} \tag{5}$$

where λ_m is the wave-length of maximum reflecting power, ϵ is the electrostatic dielectric constant; K, the contribution of λ_0 to the dielectric constant, is, for the cases we consider, diatomic crystals of the regular system,

$$K = \frac{F^2 M_1 M_2}{\pi c^2 (M_1 + M_2)} \frac{\lambda_0^2}{V}, \tag{5a}$$

F being the Faraday constant, c the velocity of light, M_1 and M_2 the atomic weights of the two kinds of ions.

We will now consider the effect of volume changes on λ_m; from (5) and (5a) we have

$$\frac{d\lambda_m}{dV} = \frac{\lambda_m}{\lambda_0}\left[1 - \frac{\lambda_m^2 K(6\epsilon - 4)}{\lambda_0^2(6\epsilon - 6K - 4)^2}\right]\frac{d\lambda_0}{dV} + \frac{\lambda_m^3 K}{\lambda_0^2(6\epsilon - 6K - 4)^2}\left(\frac{6\epsilon - 4}{V} + 6\frac{d\epsilon}{dV}\right). \tag{6}$$

We see, therefore, that, to know the change of the residual ray maximum with changing volume, we must know not only $\frac{d\lambda_0}{dV}$ but also the change of dielectric constant with volume, $\frac{d\epsilon}{dV}$. This we will now consider separately.

The Lorentz-Lorenz equation stated that $\frac{\epsilon - 1}{\epsilon + 2}$ for a given substance is proportional to its density,[9] and this relation holds for crystals of the sodium chloride type (Ref. 1, p. 773). We have, then,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\text{const.}}{V},$$

whence

$$\frac{d\epsilon}{dV} = -\frac{(\epsilon - 1)(\epsilon + 2)}{3V}. \tag{5b}$$

Substituting this in (6),

$$\frac{d\lambda_m}{dV} = \frac{\lambda_m}{\lambda_0}\left[1 - \frac{\lambda_m^2 K(6\epsilon - 4)}{\lambda_0^2(6\epsilon - 6K - 4)^2}\right]\frac{d\lambda_0}{dV} - \frac{\lambda_m^3 K\epsilon(\epsilon - 2)}{\lambda_0^2 V(6\epsilon - K - 4)^2}. \tag{7}$$

Equations (6) and (7) are, obviously, independent of any particular form of $d\lambda_0/dV$, and apply to Zwicky's evaluation of the pressure change of λ_0 as well as to our equations (2), (3) and (4).

From (2) we have

$$\frac{d\lambda_m}{dV} = \frac{\lambda_m}{\lambda_0}(1 - X)\frac{d\lambda_0}{dV}, \tag{8}$$

where

$$X = \frac{\lambda_m^2 K}{\lambda_0^2(6\epsilon - 6K - 4)^2}\left(6\epsilon - 4 + \frac{6\epsilon(\epsilon - 2)}{n + 1}\right). \tag{8a}$$

Using (3) and (4), we get from (8)

$$\left(\frac{\partial\lambda_m}{\partial T}\right)_P = \frac{\lambda_m}{\lambda_0}(1 - X)\left(\frac{\partial\lambda_0}{\partial T}\right)_P \tag{9}$$

$$\left(\frac{\partial\lambda_m}{\partial P}\right)_T = \frac{\lambda_m}{\lambda_0}(1 - X)\left(\frac{\partial\lambda_0}{\partial P}\right)_T \tag{10}$$

Table 2 shows the calculated variations of the reflection bands for 100°C. or 100 atmospheres change.

TABLE 2

VARIATIONS OF REFLECTION BANDS WITH TEMPERATURE AND PRESSURE

SALT	$\lambda_m^{(7)}$ μ	$\epsilon^{(1)}$	$K^{(1)}$	$\frac{\lambda_m}{\lambda_0}(1-x)$	$\pm\Delta\lambda_m$ FOR $\pm$100°C. CHANGE μ	$-\Delta\lambda_m$ FOR 100 ATM. CHANGE μ
NaCl	52.0	5.82	3.51	0.043	0.058	0.0022
KCl	63.4	4.75	2.59	0.25	0.33	0.019
KBr	82.6	4.66	2.30	0.40	0.70	0.045
KI	94.1	5.10	2.44	0.49	1.29	0.083

We see that, for the same volume change, the shift in the reflection band is a fraction of the shift in the absorption band. In the case of rock-salt, the fraction is sufficiently small to promise particular difficulties in the measurement of the temperature as well as the pressure shift of reflection maximum. The temperature shifts of the reflection bands of KCl, KBr and KI appear measurable, however, though it must be remembered that the prediction of shifts in reflection bands depends on values of the dielectric constants. However, the relations reported here and the magnitudes of the predicted shifts warrant attempts to measure the effect of volume changes on both λ_0 and λ_m.[10]

It is expected to develop these considerations at greater length elsewhere.

* NATIONAL RESEARCH FELLOW.

[1] M. Born, *Atomtheorie des festen Zustandes.*

[2] Zwicky, *Phys. Rev.*, **29**, 579 (1927).

[3] E. Grüncisen, *Conseil de Physique Solvay*, **1913.**

[4] L. G. Carpenter and L. G. Stoodley, *Phil. Mag.*, **5**, 823, 1928.

[5] T. H. Havelock, *Proc. Roy. Soc.*, **105,** 488, 1924.

[6] J. E. Lennard-Jones and B. M. Dent, *Ibid.*, **112,** 230, 1926.

[7] Rubens, *Berl. Ber.*, **1917.**

[8] Landolt-Börnstein, 5, *Auf., Erganzungsband.*

[9] Lorentz, *Theory of Electrons*, p. 145, **1923.**

[10] Professor K. F. Herzfeld has pointed out to me that if one starts from the exact theory instead of from the Carpenter-Stoodley equation (1) as above, the expression $(n + 1)$ is replaced by $(n + 3)$. This would increase $\frac{d\lambda_0}{dV}$ and $\frac{d\lambda_m}{dV}$ about 15 to 20%.